Certification Report

Certified Reference Material

BAM-M113

Lead alloy PbCaSn

June 2024

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Summary

This report describes preparation, analysis and certification of the lead reference material BAM-M113. The certified reference material (CRM) is available in the form of discs (ca. 38 mm diameter and 38 mm height). It is intended for establishing and checking the calibration of optical emission spectrometry for the analysis of samples of similar matrix composition. It is also suitable for validation of wet chemical analysis methods.
The following mass fractions and uncertainties have been certified:

Certified Values

Element	Mass fraction [1] in %	Uncertainty [2] in %
Ca	0.124	0.005
Sn	1.047	0.019
Bi	0.0194	0.0008
Al	0.0145	0.0009
	in mg/kg	**in mg/kg**
Ag	64.7	1.5
Cu	18.9	0.8
Fe [3]	1.0	0.5
Sb	5.4	1.0

[1] Unweighted mean value of the means of accepted sets of data (consisting of at least 3 single results), each set being obtained by a different laboratory and/or a different method of measurement.
[2] Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement, (GUM, ISO/IEC Guide 98-3:2008).
[3] The mean value is estimated using the marginal likelihood for the mean (see below)

Element	Mass fraction (limits) [4] in mg/kg	Uncertainty [5] (error probability)
As	< 1	0.05
Cr	< 0.5	0.05
Mn	< 0.5	0.05
Se	< 1	0.05

[4] The upper limit is estimated by calculating the 95% quantile of the marginal likelihood distribution (see below)
[5] The uncertainty refers to the probability of errors or in other words the significance level. A commonly used significance level is 0.05, which means that the probability for an error (i.e., the true value is outside of the given range) is 5%,

This report contains detailed information on the preparation of the CRM as well as on homogeneity investigations and on the analytical methods used for certification.
The certified values are based on the results of twelve laboratories which participated in the certification inter-laboratory comparison.

Content

List of abbreviations
(if not explained elsewhere)

CRM	certified reference material
FAAS	flame atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
SOES	spark optical emission spectrometry
M	mean value
n	number of accepted data sets
s	standard deviation of an individual data set (within laboratory deviation)
s_M	standard deviation of laboratory means
s_{rel}	relative standard deviation of an individual data set (rel. within laboratory deviation)
$\bar{s}_i$	square root of averaged within laboratory variances
M_i	single values measured at participating laboratories
I	ICP-OES (Tables 2 – 13)
I(R)	ICP-OES, revised value (Tables 2 – 13)
IMS	ICP-MS (Tables 2 – 13)
A	FAAS (Tables 2 – 13)
G	gravimetry (Tables 2 – 13)

1. Introduction

In the metal-producing and metal-working industry mainly spark emission spectrometry (SOES) is used for reception inspection of raw materials, e.g. scrap, for quality control of end products and production control. This time-saving analytical technique requires suitable reference materials for calibration and recalibration. The certified reference material BAM-M113 is a lead alloy based on lead-calcium. Its element contents represent the element contents of ERM-EB101a and ERM-EB102a which will be replaced by BAM-M113. The main field of application for PbCa alloys is the production of lead emitters for use in lead-acid batteries.

The reference material for BAM-M113 was produced together with the working group „Lead" of the Committee of Chemists within the Society of Metallurgists und Miners (GDMB). Participating laboratories were recruited from this group. Since all these laboratories are highly experienced with lead analysis and had participated in earlier interlaboratory comparisons, there was no preceding proficiency test for qualification necessary.

Certification was carried out on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

2. Companies/laboratories involved

Manufacturing of the material:

– SUS Nell, Oberhausen, Germany

Test for homogeneity:

– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

Participants in the certification inter-laboratory comparison:

Aurubis AG, Hamburg, Germany
BAE Batterien GmbH, Berlin, Germany
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
Nyrstar Stolberg, Stolberg, Germany
Clarios Germany GmbH & Co. KGaA, Hannover, Germany
Clarios, BTC Labs, Glendale WI, United States
Clarios Mexico, Monterrey Mexico
Clarios Zwickau GmbH & Co. KG, Zwickau, Germany
Ecobat Resources Freiberg GmbH, Freiberg, Germany
Hoppecke Batterien GmbH & Co. KG, Brilon-Hoppecke, Germany
Raghavendra Spectro Metallurgical Laboratory, Bangalore, India
TU Clausthal, Clausthal-Zellerfeld, Germany

Statistical evaluation of the data:

– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

3. Candidate material

An alloyed lead (1 % Sn, 0.02 % Bi, 0.08 % Ca) was used as basic material for the preparation of the candidate material. This material was milled, melted and doped with the desired impurities by SUS Nell, Oberhausen. Nine sub-batches were produced (1 – 9), from which cylinders were casted.
In total, 330 discs (after removal of sub-batch 2, see §4) of BAM-M113 with a diameter of ca. 38 mm and 38 mm height were obtained.

4. Homogeneity testing

Possible reasons for an inhomogeneous distribution of elements in the raw material may be a change of the composition of the melt during the casting procedure because some elements may volatize or because of possible segregation during the solidification of the material. Since the raw material was produced by casting of a rod, concentration gradients can occur over the length of the rod (axial) as well as over the area of the rod (radial, see Figure 1):

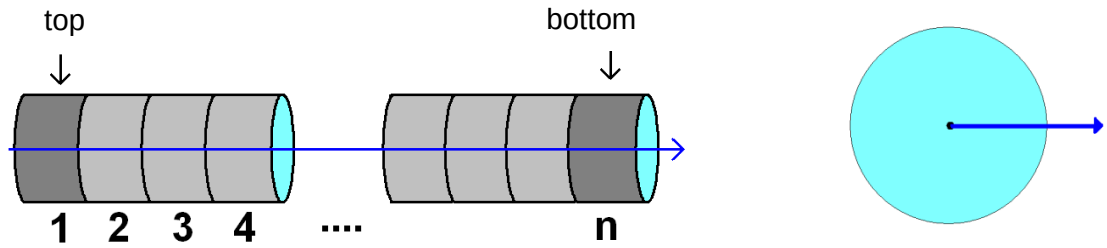


Fig. 1: Axial and radial composition gradient

Therefore, it is necessary to investigate the raw material for both axial and radial inhomogeneities. Radial as well as axial homogeneity testing of the candidate material was done using spark emission spectrometry. For the axial homogeneity study 18 discs (one from the top and one from the bottom of each sub-batch) of BAM-M113 were investigated (4 sparks per disc for homogeneity between different discs (sub-batches)). As a result of this homogeneity test all discs of sub-batch 2 were withdrawn, because its composition differed slightly from the other sub-batches (see Annex 1 and 2).

The estimate of analyte-specific inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [4] using Eq. (1) and Eq. (2):

$$s_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \qquad (1)$$

$$u^{*}_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

where:

MS_{among}	mean of squared deviations between discs (from 1-way ANOVA, see Annex 1)
MS_{within}	mean of squared deviations within one disc (from 1-way ANOVA)
n	number of replicate measurements per disc
N	number of discs selected for homogeneity study

s_{bb} signifies the between-discs standard deviation whereas u^*_{bb} denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). In any case the larger of the two values was used as $u_{bb}(1)$ for inhomogeneity over the length. Eq. (1) does not apply if MS_{within} is larger than MS_{among}.

In addition to the tests performed over the length of the rods six discs were tested for homogeneity over the area (possible segregation from the outer part to the centre) in BAM. To perform this test SOES analysis was carried out in circles (outer circle: 4 sparks, 4 inner circle: 4 sparks; centre: 3-4 sparks, see Figure 2).

Fig. 2: Measurement scheme for radial homogeneity testing

The analyte-specific within-disc uncertainty component $u_{bb}(2)$ was calculated in the same way as for as $u_{bb}(1)$. From the six discs the median of the higher components is used for uncertainty calculation.

Annexes 2 and 3 show the results of the homogeneity calculations.

5. Characterisation study

5.1 Analytical methods

Twelve laboratories participated in the certification inter-laboratory comparison. For some elements part of the laboratories used more than one analytical method reporting more than one data set.
The laboratories were asked to analyse six subsamples. They were free to choose any suitable analytical method. Table 1 shows the analytical methods used by the participating laboratories.
For all analytical methods where a calibration was necessary this calibration was performed using liquid standard solutions. All participating laboratories were asked to use only standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

Table 1: Analytical procedures used by the participating laboratories (* accr. to ISO/IEC 17025)

Lab-No.	Element	Sample mass	Sample pretreatment	Analytical method
1	Ca, Sn, Bi, Al	0.25 g	Dissolution HNO_3/HF/HCl	ICP-OES with calibration with commercial solutions (Spex certified)
	Cu	1 g	Dissolution HNO_3/HF/HCl	ICP-OES with calibration with commercial solutions (Spex certified)
	Ag, Sb, Se, Cr, Mn, As, Fe	0.5 g	Dissolution HNO_3/HF/HCl	ICP-MS with calibration with commercial solutions (Environmental Calibration Standard)
2*	Ca, Sn, Bi, Al, Ag, Cu	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Merck certipur)
	Sn	10 g	Dissolution with HNO_3	Gravimetry as SnO_2
	Ca, Ag, Cu	10 g	Dissolution with HNO_3, separation of SnO_2 and $Pb(NO_3)_2$	FAAS, calibration with commercial solutions (Merck certipur)
	Fe	10 g	Dissolution with HNO_3, separation of SnO_2	Spectrophotometry with bipyridine
3	Ca, Sn, Bi, Al, Ag, Cu, Cr, Mn, Fe		Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Merck certipur)
4	Ca, Sn, Bi, Al, Ag, Cu, Sb, Se, Cr, Mn, As, Fe	1 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Merck certipur)
5	Ca, Sn, Bi, Al, Ag, Cr, Mn	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Merck certipur)
	Cu, Sb, Se, As, Fe	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Analytichem)
6	Ca, Sn, Bi, Al, Ag, Cu, Sb, Se, Cr, Mn, As, Fe	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with matrix matched standards with commercial solutions (Bernd Kraft)
7	Ca, Bi, Al, Ag, Cu, Sb, Fe	1 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck)
	Sn	1 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with matrix matched standards, calibration with commercial solutions (Bernd Kraft)
10	Ca, Sn, Al, Ag, Cu, Fe	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Merck)
11*	Ca, Sn, Bi, Al, Ag, Cu, Sb, Se, Cr, Mn, As, Fe	1.7 g	Dissolution with HNO_3 and traces of tartaric acid	ICP-OES, calibration with commercial solutions (Merck)
	Sn	1 g	Dissolution with HNO_3 and traces of tartaric acid	ICP-OES, calibration with commercial solutions (Merck)
12	Ca, Sn, Bi, Al, Ag, Cu, Sb, Se, Cr, Mn, As, Fe	1.7 g	Dissolution with tartaric acid/HNO_3	ICP-OES, with matrix matched standards, calibration with commercial solutions
13	Ca, Sn, Bi, Al	0.5 g	Dissolution with HNO_3/fluoroboric acid	ICP-OES, calibration with matrix matched standards with commercial solutions (XAMSA)
	Ag, Cu, Sb, Se, Cr, Mn, As, Fe	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with matrix matched standards with commercial solutions (XAMSA)
14	Ca	0.2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with commercial solutions (Merck)

5.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are listed in Tables 2 to 13. The measured mass fractions are mostly provided as quantitative numeric values. Yet, for some elements part of the laboratories provided censored values, which indicated that a mass fraction is below a certain threshold (e.g., <0.1 mg/kg). The tables show the single results (M_i) of each laboratory, and for the quantitative values the respective laboratories' mean values (M), absolute and relative intra-laboratory standard deviation (s and s_{rel}, respectively), the standard deviation of laboratory means (s_M), and in addition the square root of mean of variances of data sets under repeatability conditions ($\bar{s}_i$) where n is the number of accepted data sets.
In the related figures the continuous line marks mean of the laboratories' means (which corresponds to the certified value, if all laboratories provided quantitative values), the broken lines form the upper and lower limits of the range $M \pm 1s$, the standard deviation calculated from the laboratories' means.
Further, for each laboratory its mean value and single standard deviation is given. Outliers which have been excluded are highlighted in yellow.

Table 2: Results for Ca in BAM-M113

Lab./Meth.	10/I	5/I	1/I	12/I	2/I	4/I	2/A	7/I	3/I	14/I	6/I	11/I	13/I		
M_i [%]	0.0940	0.118	0.119	0.114	0.1221	0.119	0.123	0.121	0.124	0.126	0.125	0.132	0.134		*n*
	0.0900	0.118	0.118	0.120	0.1199	0.124	0.127	0.124	0.124	0.132	0.127	0.133	0.134		13
	0.0810	0.119	0.119	0.120	0.1204	0.122	0.123	0.123	0.126	0.124	0.126	0.132	0.127		
	0.1150	0.119	0.120	0.121	0.1217	0.123	0.118	0.122	0.127	0.125	0.129	0,1325	0.128		
	0.1130	0.119	0.121	0.124	0.1214	0.121	0.117	0.125	0.128	0.125	0.129	0.132	0.129		
	0.1130	0.119	0.120	0.121	0.1215	0.124	0.129	0.122	0.123		0.132	0.132	0.131		
													0.136		
													0.136		
													0.135		
M [%]	**0.1010**	**0.1187**	**0.1195**	**0.1202**	**0.1212**	**0.1222**	**0.1229**	**0.1229**	**0.1253**	**0.1264**	**0.1277**	**0.1320**	**0.1322**		**0.1243**
s [%]	0.0145	0.0005	0.0010	0.0031	0.0008	0.0019	0.0047	0.0015	0.0021	0.0032	0.0026	0.0004	0.0034	s_M [%]	0.0046
														$\bar{s}_i$ [%]	0.0025
s_{rel}	0.14375	0.00435	0.00878	0.02572	0.00692	0.01519	0.03848	0.01253	0.01675	0.02539	0.02046	0.00315	0.02577		0.03666

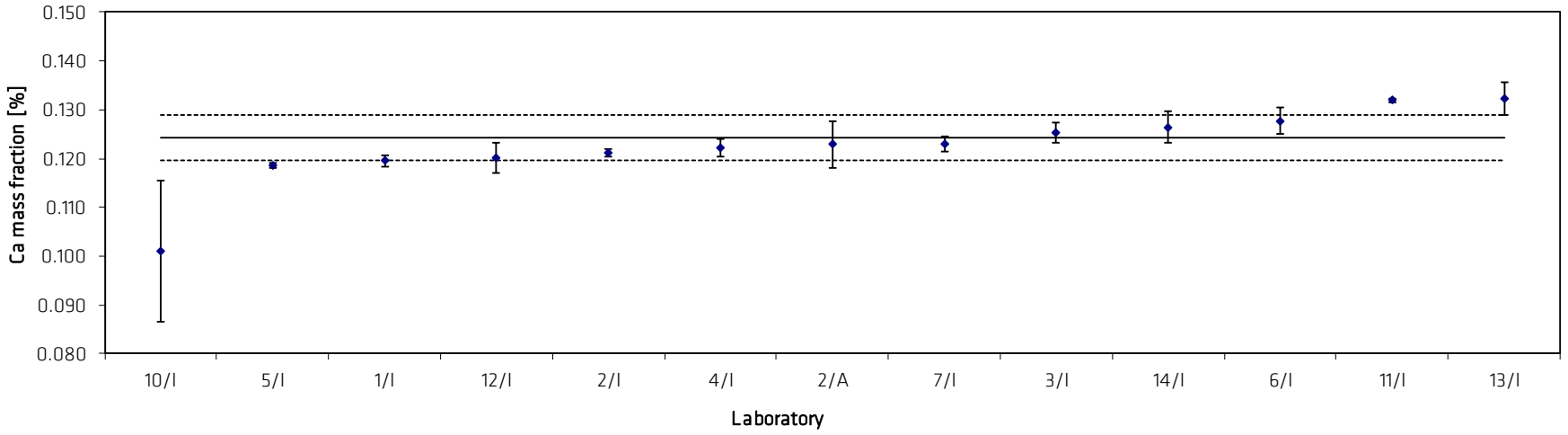


Table 3: Results for Sn in BAM-M113

Lab./Meth.	6/I	14/I	5/I	7/I	11/I	10/I	1/I	2/I	4/I	2/G	12/I	3/I	13/I		
M_i [%]	0.819	0.887	1.011	1.023	1.024	1.0390	1.050	1.045	0.976	1.049	1.048	1.068	1.087		*n*
	0.852	0.893	1.017	1.039	1.023	1.0300	1.040	1.033	1.059	1.058	1.071	1.067	1.085		13
	0.838	0.849	1.023	1.035	1.023	0.9650	1.040	1.042	1.051	1.049	1.078	1.079	1.093		
	0.845	0.879	1.029	1.011	1.023	1.0640	1.040	1.046	1.057	1.028	1.078	1.090	1.099		
	0.844	0.875	1.018	1.011	1.023	1.0770	1.040	1.042	1.053	1.055	1.083	1.098	1.085		
	0.837		1.019	1.005	1.024	1.0740	1.040	1.050	1.071	1.029	1.080	1.070	1.084		
													1.083		
													1.087		
													1.082		
***M* [%]**	**0.839**	**0.877**	**1.020**	**1.021**	**1.023**	**1.042**	**1.042**	**1.043**	**1.045**	**1.045**	**1.073**	**1.079**	**1.087**		**1.047**
s [%]	0.0111	0.0169	0.0061	0.0140	0.0001	0.0420	0.0041	0.0055	0.0341	0.0132	0.0128	0.0128	0.0054	s_M [%]	0.0232
														$\overline{s}_i$ [%]	0.0184
s_{rel}	0.01325	0.01932	0.00594	0.01371	0.00011	0.04031	0.00392	0.00529	0.03263	0.01262	0.01191	0.01182	0.00501		0.02215

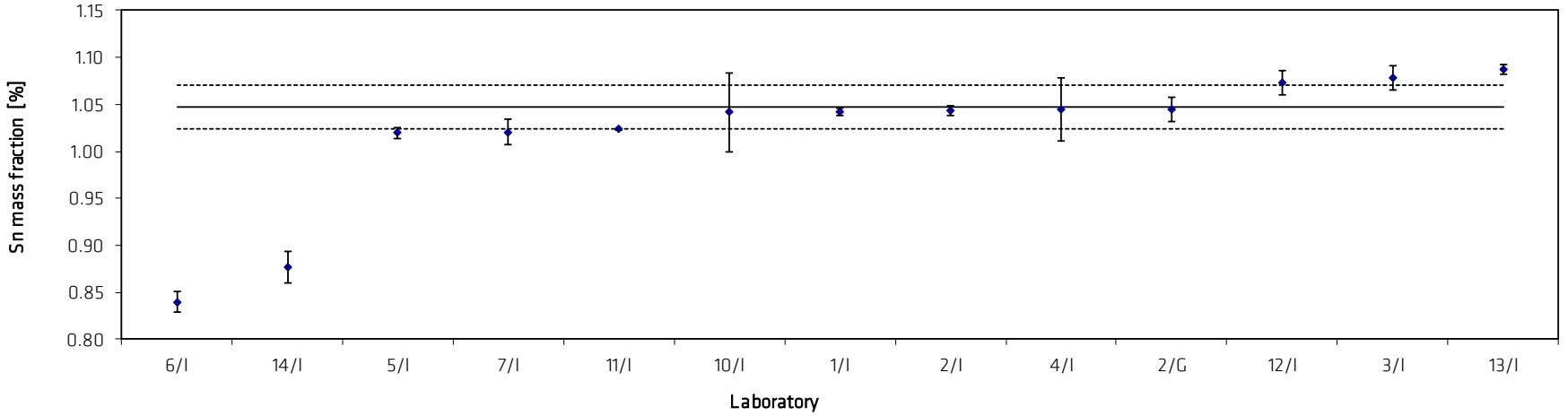


Table 4: Results for Bi in BAM-M113

Lab./Meth.	12/I	6/I	11/I	2/I	5/I	1/I	13/I	3/I	7/I	4/I		
M_i [%]	0.0170	0.0180	0.0189	0.0193	0.019	0.0200	0.0202	0.0200	0.0202	0.0197		*n*
	0.0172	0.0183	0.0192	0.0192	0.020	0.0198	0.0199	0.0201	0.0206	0.0211		10
	0.0171	0.0180	0.0186	0.0191	0.020	0.0202	0.0199	0.0202	0.0209	0.0212		
	0.0175	0.0180	0.0182	0.0188	0.019	0.0200	0.0203	0.0206	0.0201	0.0219		
	0.0174	0.0180	0.0187	0.0187	0.020	0.0201	0.0203	0.0206	0.0202	0.0213		
	0.0173	0.0176	0.0185	0.0192	0.020	0.0200	0.0201	0.0199	0.0213	0.0201		
							0.0202					
							0.0205					
							0.0200					
***M* [%]**	**0.0173**	**0.0180**	**0.0187**	**0.0191**	**0.0197**	**0.0200**	**0.0201**	**0.0202**	**0.0206**	**0.0209**		**0.0194**
s [%]	0.0002	0.0002	0.0003	0.0002	0.0005	0.0001	0.0002	0.0003	0.0005	0.0008	s_M [%]	0.0012
											$\bar{s}_i$ [%]	0.0004
s_{rel}	0.01028	0.01239	0.01836	0.01275	0.02626	0.00664	0.01036	0.01480	0.02318	0.03981		0.06045

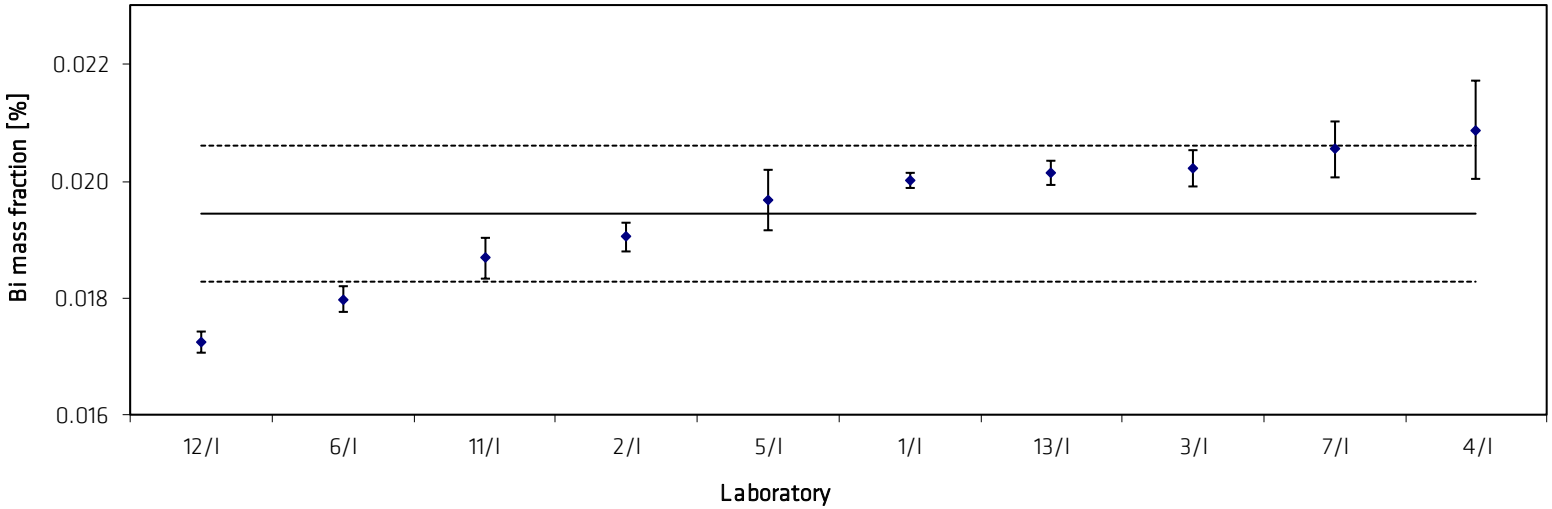


Table 5: Results for Al in BAM-M113

Lab./Meth.	12/I	5/I(R)	10/I	2/I	1/I	4/I	7/I	11/I	6/I	3/I	14/I	13/I		
M_i [%]	0.0122	0.0128	0.0117	0.0142	0.0145	0.0146	0.0144	0.0145	0.0147	0.0149	0.016	0.0163		*n*
	0.0119	0.0131	0.0118	0.0141	0.0145	0.0146	0.0147	0.0146	0.0152	0.0149	0.016	0.0160		12
	0.0118	0.0129	0.0123	0.0142	0.0146	0.0146	0.0149	0.0148	0.0154	0.0151	0.016	0.0161		
	0.0119	0.0130	0.0165	0.0143	0.0145	0.0146	0.0144	0.0145	0.0150	0.0153	0.016	0.0164		
	0.0119	0.0129	0.0162	0.0142	0.0143	0.0146	0.0147	0.0149	0.0149	0.0154	0.017	0.0162		
	0.0118	0.0131	0.0165	0.0145	0.0144	0.0145	0.0148	0.0152	0.0144	0.0147		0.0161		
												0.0160		
												0.0164		
												0.0160		
M [%]	**0.0119**	**0.0130**	**0.0142**	**0.0143**	**0.0145**	**0.0146**	**0.0147**	**0.0148**	**0.0149**	**0.0150**	**0.0162**	**0.0162**		**0.0145**
s [%]	0.0001	0.0001	0.0025	0.0001	0.0001	0.0000	0.0002	0.0003	0.0003	0.0003	0.0004	0.0002	s_M [%]	0.0012
													$\bar{s}_i$ [%]	0.0007
s_{rel}	0.01208	0.00803	0.17346	0.00967	0.00714	0.00313	0.01415	0.01857	0.02163	0.01756	0.02761	0.01046		0.08159

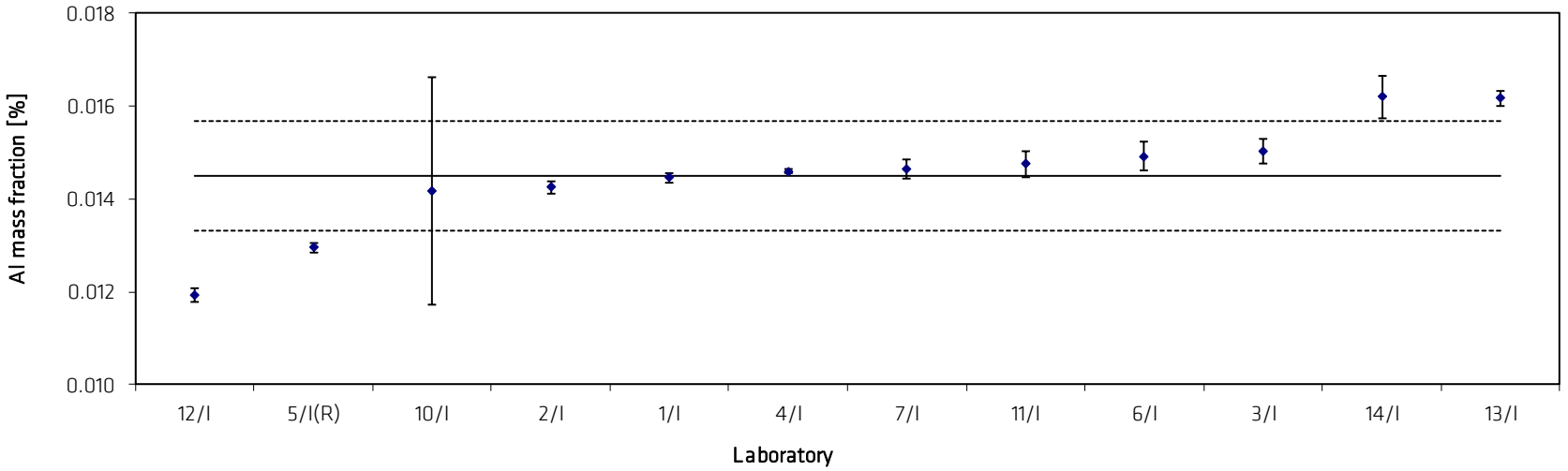


Table 6: Results for Ag in BAM-M113

Lab./Meth.	6/I	12/I	5/I	13/I	1/IMS	2/A	2/I	10/I	7/I	3/I	4/I	11/I(R)		
M_i [mg/kg]	58.8	62.8	62.9	64.2	64.0	62.4	65.2	67.0	67.2	65.9	68.2	75.0		*n*
	61.0	62.7	63.1	63.0	63.0	66.5	64.5	67.0	67.6	66.3	68.7	76.0		12
	60.4	61.9	63.7	63.6	65.0	64.4	65.1	68.0	66.9	66.8	69.0	75.0		
	60.3	63.3	63.4	65.1	65.0	63.2	65.1	63.4	67.3	67.7	68.9	75.0		
	59.6	63.2	63.0	64.3	64.0	63.7	65.1	63.1	67.2	68.0	69.2	74.0		
	59.6	62.8	63.3	63.7	64.0	65.9	65.4	63.7	63.3	65.9	69.6	75.0		
				63.7										
				65.5										
				63.8										
M [mg/kg]	**60.0**	**62.8**	**63.3**	**64.1**	**64.2**	**64.4**	**65.1**	**65.4**	**66.6**	**66.8**	**68.9**	**75.0**		**64.7**
s [mg/kg]	0.78	0.49	0.30	0.77	0.75	1.59	0.30	2.18	1.62	0.91	0.47	0.63	s_M [mg/kg]	2.35
													$\bar{s}_i$ [mg/kg]	1.09
s_{rel}	0.013	0.008	0.005	0.012	0.012	0.025	0.005	0.033	0.024	0.014	0.007	0.008		0.036

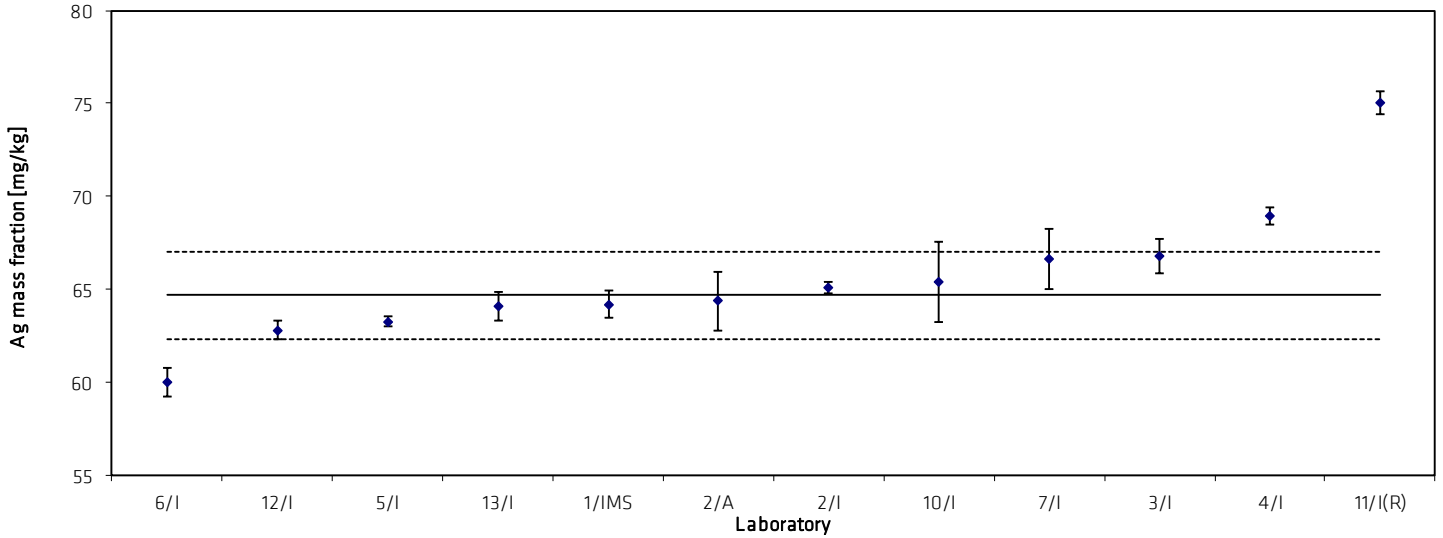


Table 7: Results for Cu in BAM-M113

Lab./Meth.	2/I	2/A	5/I	6/I	13/I	7/I	12/I	3/I	4/I	1/I	10/I	11/I		
M_i [mg/kg]	17.0	17.1	17.2	17.4	18.9	19.4	19.1	19.2	20.0	19.9	21.0	20.0		*n*
	17.0	17.8	17.3	18.1	18.5	19.7	19.6	19.2	19.7	20.3	20.0	23.0		12
	17.0	17.0	17.5	17.9	18.6	19.2	19.2	19.4	19.6	20.1	21.0	19.0		
	17.0	16.4	17.6	17.8	19.1	19.5	19.7	19.9	19.2	19.7	21.2	22.0		
	17.0	17.2	17.5	17.5	18.9	19.5	20.0	20.0	20.1	19.5	19.5	22.0		
	17.0	17.4	17.5	17.6	18.8	18.1	19.2	19.1	19.4	20.1	19.1	21.0		
					18.7									
					19.3									
					18.8									
M [mg/kg]	**17.0**	**17.2**	**17.4**	**17.7**	**18.8**	**19.2**	**19.5**	**19.5**	**19.6**	**19.9**	**20.3**	**21.2**		**18.9**
s [mg/kg]	0.00	0.46	0.16	0.26	0.24	0.58	0.34	0.39	0.32	0.30	0.91	1.47	s_M [mg/kg]	1.34
													$\bar{s}_i$ [mg/kg]	0.59
s_{rel}	0.000	0.027	0.009	0.014	0.013	0.030	0.018	0.020	0.017	0.015	0.045	0.070		0.071

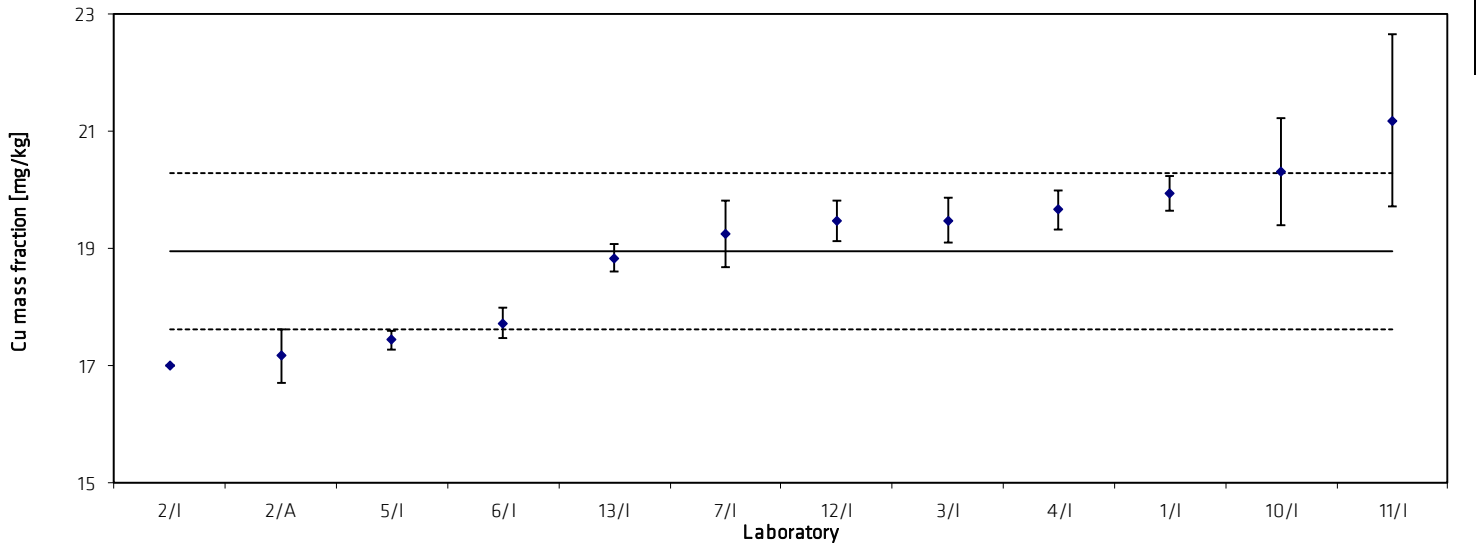


Table 8: Results for Sb in BAM-M113

Lab./Meth.	6/I	13/I	1/IMS(R)	5/I	12/I	7/I	11/I	4/I		
M_i [mg/kg]	<0.2	<0.5	3.7	4.7	5.5	4.7	5.0	8.7		*n*
	<0.2	<0.5	3.9	4.5	5.5	5.5	6.0	7.1		8
	<0.2	<0.5	4.0	4.6	5.2	5.0	5.0	7.3		
	<0.2	<0.5	4.0	4.6		6.7	7.0	7.2		
	<0.2	<0.5	4.2	4.7		6.4	6.0	7.1		
	<0.2	<0.5	4.1	4.7		4.6	6.0	6.9		
		<0.5								
		<0.5								
		<0.5								
M **[mg/kg]**	**<0.2**	**<0.5**	**3.97**	**4.62**	**5.40**	**5.48**	**5.83**	**7.36**		**5.44**
s [mg/kg]			0.183	0.075	0.173	0.889	0.753	0.647	s_M [mg/kg]	1.158
									$\bar{s}_i$ [mg/kg]	0.554
s_{rel}			0.046	0.016	0.032	0.162	0.129	0.088		0.213

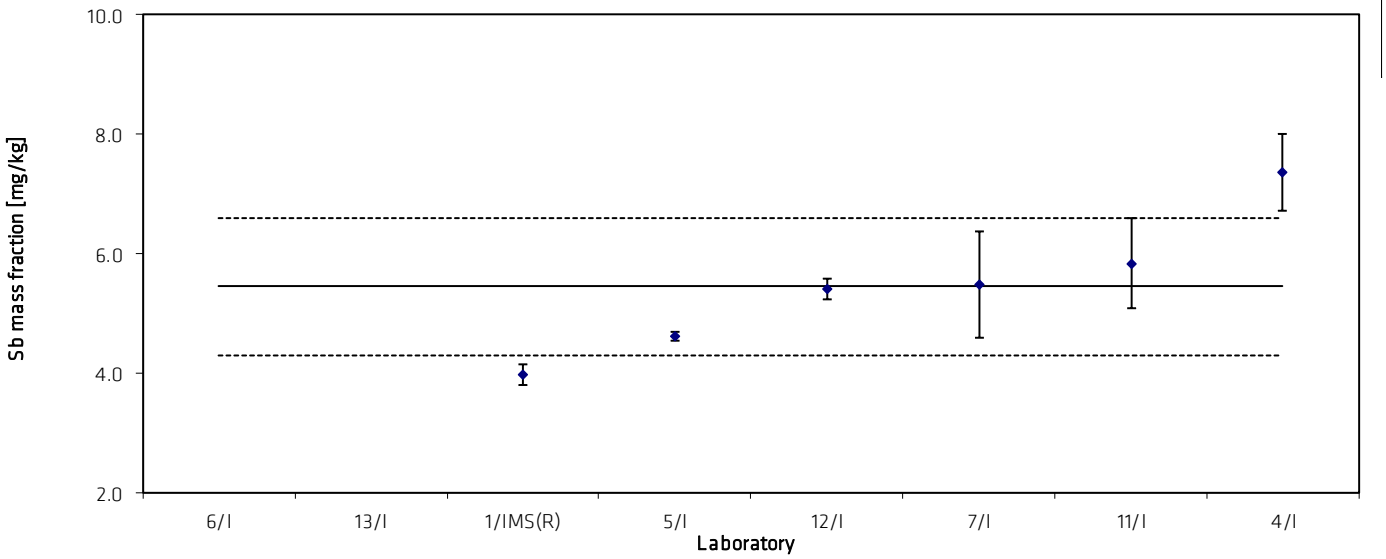


Table 9: Results for Fe in BAM-M113

Lab./Meth.	6/I	5/I	2/P	3/I	12/I	1/IMS	4/I	7/I	11/I(R)	13/I	10/I		
M_i [mg/kg]	<0.03	0.36	0.53	0.7	1.03	<1	<1	1.4	1.50	2.03	2.0		*n*
	<0.03	0.39	0.51	0.7	0.33	<1	<1	1.5	1.50	2.06	2.0		11
	<0.03	0.36	0.52	0.7	0.86	<1	<1	1.2	1.80	1.94	2.0		
	<0.03	0.35	0.55	0.7	0.80	<1	<1	1.3	1.20	2.05	1.8		
	<0.03	0.44	0.53	0.6	1.11	<1	<1	1.2	1.50	1.41	1.6		
	<0.03	0.42	0.50	0.6		<1	<1	2.0	1.50	1.27	1.9		
							<1			1.23			
							<1			1.34			
							<1			1.38			
M [mg/kg]	**<0.03**	**0.39**	**0.52**	**0.67**	**0.83**	**<1**	**<1**	**1.43**	**1.50**	**1.63**	**1.89**		**1.11**
s [mg/kg]		0.037	0.018	0.052	0.304			0.301	0.190	0.374	0.148	s_M [mg/kg]	0.570
												$\bar{s}_i$ [mg/kg]	0.219
s_{rel}		0.095	0.033	0.077	0.368			0.210	0.126	0.229	0.078		0.515

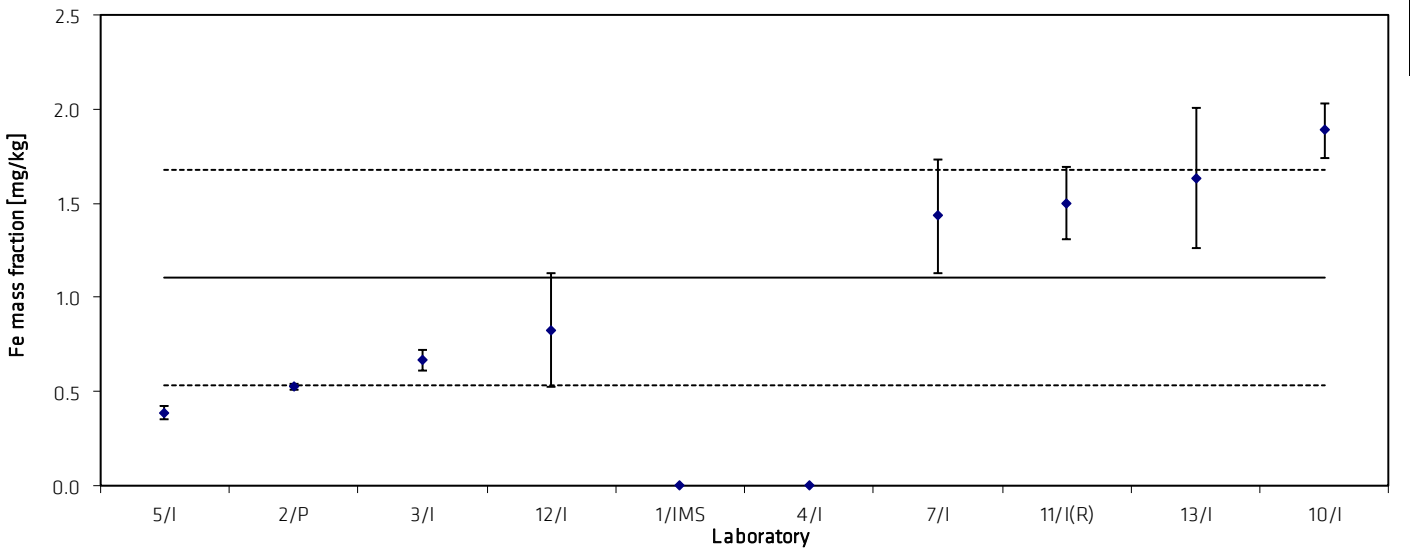


Table 10: Results for Se in BAM-M113

Lab./Meth.	1/IMS	5/I	13/I	12/I	6/I	11/I	4/I		
M_i [mg/kg]	<0.3	<0.44	<0.5	<0.7	1.0	<1	<2		*n*
	<0.3	<0.44	<0.5	<0.7	1.0	<1	<2		7
	<0.3	<0.44	<0.5	<0.7	0.8	<1	<2		
	<0.3	<0.44	<0.5	<0.7	1.0	<1	<2		
	<0.3	<0.44	<0.5	<0.7	1.0	<1	<2		
	<0.3	<0.44	<0.5	<0.7	1.0	<1	<2		
			<0.5	<0.7			<2		
			<0.5	<0.7			<2		
			<0.5	<0.7			<2		
M [mg/kg]	**<0.3**	**<0.44**	**<0.5**	**<0.7**	**0.94**	**<1**	**<2**		**< 1**
s [mg/kg]					0.074			s_M [mg/kg]	
								$\bar{s}_i$ [mg/kg]	
s_{rel}					0.079				

Table 11: Results for Cr in BAM-M113

Lab./Meth.	5/I	1/IMS	6/I	3/I	12/I	13/I	11/I	4/I		
M_i [mg/kg]	<0.1	<0.1	0.15	0.2	0.22	<0.5	<1	<1		*n*
	<0.1	<0.1	0.12	0.2	0.23	<0.5	<1	<1		8
	<0.1	<0.1	0.18	0.2	0.22	<0.5	<1	<1		
	<0.1	<0.1	0.13	0.3	0.24	<0.5	<1	<1		
	<0.1	<0.1	0.13	0.2	0.20	<0.5	<1	<1		
	<0.1	<0.1	0.16	0.2		<0.5	<1	<1		
						<0.5		<1		
						<0.5		<1		
						<0.5		<1		
M [mg/kg]	**<0.1**	**<0.1**	**0.15**	**0.22**	**0.22**	**<0.5**	**<1**	**<1**		**< 0.5**
s [mg/kg]			0.022	0.041	0.015				s_M [mg/kg]	
									$\bar{s}_i$ [mg/kg]	
s_{rel}			0.151	0.188	0.067					

Table 12: Results for Mn in BAM-M113

Lab./Meth.	12/I	6/I	5/I	3/I	1/IMS	13/I	11/I	4/I		
M_i [mg/kg]	0.02	0.030	<0.1	0.1	0.09	<0.5	<1	<1		*n*
	0.01	0.022	<0.1	0.1	0.11	<0.5	<1	<1		8
	0.01	0.010	<0.1	0.1	0.10	<0.5	<1	<1		
	0.02	0.017	<0.1	0.1	0.11	<0.5	<1	<1		
	0.02	0.027	<0.1	0.1	0.13	<0.5	<1	<1		
	0.02	0.013	<0.1	0.1	0.13	<0.5	<1	<1		
						<0.5		<1		
						<0.5		<1		
						<0.5		<1		
***M* [mg/kg]**	**0.02**	**0.02**	**<0.1**	**0.10**	**0.11**	**<0.5**	**<1**	**<1**		**< 0.5**
s [mg/kg]	0.005	0.008		0.000	0.016				s_M [mg/kg]	
									$\bar{s}_i$ [mg/kg]	
s_{rel}	0.310	0.398		0.000	0.143					

Table 13: Results for As in BAM-M113

Lab./Meth.	6/I	1/IMS	5/I	13/I	11/I(R)	12/I	4/I		
M_i [mg/kg]	<0.18	<0.2	<0.32	<0.5	<1	1.5	<2		*n*
	<0.18	<0.2	<0.32	<0.5	<1	1.1	<2		7
	<0.18	<0.2	<0.32	<0.5	<1	1.1	<2		
	<0.18	<0.2	<0.32	<0.5	<1	2.8	<2		
	<0.18	<0.2	<0.32	<0.5	<1	1.0	<2		
	<0.18	<0.2	<0.32	<0.5	<1	3.2	<2		
				<0.5			<2		
				<0.5			<2		
				<0.5			<2		
***M* [mg/kg]**	**<0.18**	**<0.2**	**<0.32**	**<0.5**	**<1**	**1.79**	**<2**		**< 1**
s [mg/kg]						0.977			
s_{rel}						0.546			

The data (actually measured values only) was statistically evaluated to detect outlying values (Grubbs, Dixon, Cochran). The Cochran-test was performed only once. The following results were obtained:

Tab. 14: Outcome of statistical tests on the results obtained for Bi and Al

	Bi	Al
Number of data sets	10	12
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	Labs. 12 and 5
Grubbs Pair (α = 0.01)	---	---
Cochran (α = 0.01)	Lab. 4	Lab. 10
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The outliers were not removed.

Table 15: Outcome of statistical tests of results obtained for Ca in BAM-M113

	1st run	2nd run
Number of data sets	13	12
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 10	---
Dixon (α = 0.01)	---	---
Grubbs (α = 0.05)	Lab. 10	---
Grubbs (α = 0.01)	Lab. 10	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran (α = 0.01)	Lab. 10	---
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The outlier (Lab. 10, 1st run) was removed.

Table 16: Outcome of statistical tests of results obtained for Sn in BAM-M113

	1st run	2nd run	3rd run
Number of data sets	13	12	11
Scheffe's test (data compatible?)	yes	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 6	Lab. 14	---
Dixon (α = 0.01)	---	Lab. 14	---
Grubbs (α = 0.05)	Lab. 6	Lab. 14	---
Grubbs (α = 0.01)	Lab. 6	Lab. 14	---
Grubbs Pair (α = 0.05)	---	---	---
Grubbs Pair (α = 0.01)	---	---	---
Cochran (α = 0.01)	Lab. 10	Lab. 10	Lab. 10
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal	Distribution: normal

The outliers (Lab. 6, 1st run, Lab. 14, 2nd run) were removed, the Cochran outlier was not removed.

Table 17: Outcome of statistical tests of results obtained for Ag in BAM-M113

	1st run	2nd run
Number of data sets	12	11
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 11	---
Dixon (α = 0.01)	Lab. 11	---
Grubbs (α = 0.05)	Lab. 11	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran (α = 0.01)	Lab. 10	Lab. 10
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The outlier (Lab. 11, 1st run) was removed, the Cochran outlier (Lab. 10) was not removed.

Tab. 18: Outcome of statistical tests on the results obtained for Cu and Fe

	Cu	Fe
Number of data sets	12	8
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran (α = 0.01)	Lab. 11	---
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The outlier was not removed.

Table 19: Outcome of statistical tests of results obtained for Sb in BAM-M113

	Sb
Number of data sets	6
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran (α = 0.01)	---
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal

For elements, which contain quantitative values only (after outlier removal), we follow the instructions of the ISO Guide 35 [3]. The assigned characterization value is defined as the mean of all laboratory values $\mathrm{M} = \frac{M_i}{n}$, where M_i is the value assigned by the i-th laboratory and n is the number of participating laboratories.

The standard deviation of the laboratory means is estimated by $s_M = \sqrt{\frac{\sum(M_i - M)^2}{n-1}}$ and the uncertainty of the characterization value is determined by $u_{ilc} = \frac{s_M}{\sqrt{n}}$

These values are given in Table 20.
The respective combined uncertainties (u_{comb}) were calculated from the spread resulting from the certification inter-laboratory comparison (u_{ilc}) and the uncertainty contributions from possible inhomogeneity over the length ($u_{bb}(1)$) and over area ($u_{bb}(2)$) of the material using Equation 3.

$$u_{comb} = \sqrt{u_{ilc}^2 + u_{bb}^2(1) + u_{bb}^2(2)} \qquad (3)$$

Table 20: Uncertainty calculation for BAM-M113

	uncertainty contribution from									u_{bb}(rel)	
	M	n	s_M	u_{ilc}	$u_{bb}(1)$** Length	$u_{bb}(2)$** Area	u(comb)	U		Length	Area
	%		%	%	%	%	%	%			
Ca	0.124	12	0.00456	0.0013	0.0006	0.0014	0.0020	0.0041		0.4950	1.1394
Sn	1.047	11	0.02320	0.0070	0.0014	0.0060	0.0093	0.0186		0.1290	0.5707
Bi	0.0194	10	0.00118	0.0004	0.0000	0.0001	0.0004	0.00075		0.1072	0.2674
Al	0.0145	12	0.00118	0.0003	0.0003	0.0001	0.0004	0.00089		1.9414	0.4240
	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg			
Ag	64.67	11	2.350	0.7086	0.1897	0.1544	0.750	1.499		0.2934	0.2388
Cu	18.94	12	1.336	0.3857	0.0450	0.0535	0.392	0.784		0.2375	0.2827
Sb	5.44	6	1.158	0.4726	0.0943	0.0957	0.491	0.983		1.7328	1.7596
	**calculated from u_{bb}(rel): $u_{bb} = \frac{M \cdot u_{bb}(rel)}{100}$										

The expanded uncertainties U are calculated by multiplication of u_{comb} with a coverage factor of k = 2 using Equation 4.

$$U = k \cdot u_{comb} \qquad (4)$$

For elements which contain quantitative and censored values, we follow a Bayesian approach. The Bayesian approach makes use of the likelihood function, which describes the probability of observing a set of data for a certain set of model parameters. This is in our case the probability of observing the laboratory results for a given property value of the reference material and a given standard deviation for the variation between laboratories. The maximum likelihood estimator refers to the property value and standard deviation, for which the observed laboratory results have the highest probability.

We follow the general assumption that the laboratory results are normal distributed, centred at the true property value μ with a standard deviation σ. The probability that a laboratory observes a value M_i, can be obtained from the normal density function.

$$f(M_i|\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{M_i-\mu}{\sigma}\right)^2} \quad (5)$$

The probability that a laboratory measures a value below a limit of quantification Q_i is

$$F(Q_i|\mu,\sigma) = \int_{-\infty}^{Q_i} \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} dx \quad (6)$$

The likelihood function for a set of laboratory data with quantitative numeric values $M_1, \dots, M_{n_1}$ and quantification limits $Q_1, \dots, Q_{n_2}$ is

$$l\left(\mu,\sigma\middle|M_1,\dots,M_{n_1},Q_1,\dots,Q_{n_2}\right) = \prod_{i=1}^{n_1} f(M_i|\mu,\sigma) \cdot \prod_{i=1}^{n_2} F(Q_i|\mu,\sigma) \quad (7)$$

The derived likelihood function is a 2-dimensional function. It shows, which values are most likely for the property value μ and between laboratory standard deviation σ. Figure 3 shows the 2-dimensional likelihood function for Fe as an example.

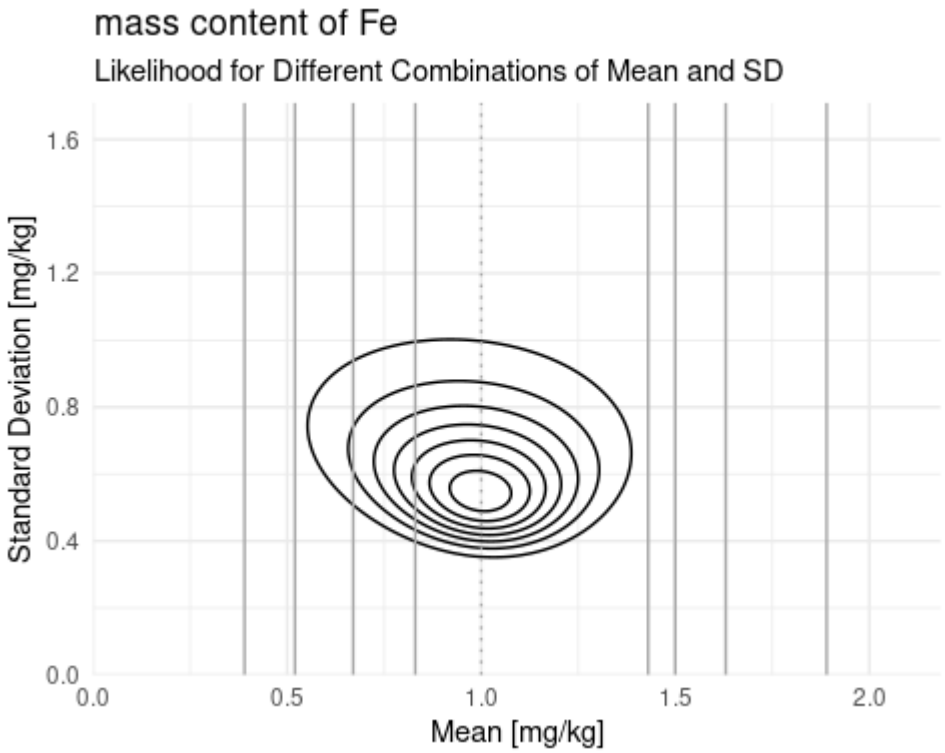


Figure 3: 2D likelihood function for the mass content of Fe, showing which values are most likely. The vertical solid lines represent the quantitative values provided by the laboratories, the vertical dotted lines represent the censored values.

At this point we are primarily interested in the true property value, rather than the between laboratory variation. Consequently, we derive a marginal distribution for μ by integration over σ.

$$l\left(\mu\middle|M_1,\dots,M_{n_1},Q_1,\dots,Q_{n_2}\right) = \int_0^{\infty} \prod_{i=1}^{n_1} f(M_i|\mu,\sigma) \cdot \prod_{i=1}^{n_2} F(Q_i|\mu,\sigma)\, d\sigma \quad (8)$$

By normalizing the marginal likelihood for μ, we receive a probability distribution for the true property value (see Fig. 4). From this probability distribution we can derive a 95% interval for true property value. We decided that at least 5 quantitative values from independent laboratories are required, to provide a reliable quantitative value and a respective uncertainty for the mass content of the considered element. If less than 5 laboratories report quantitative values, we provide a censored value, which is with 95% an upper bound for the mass content of the considered element.

After outlier removal, for the mass content of Fe 8 laboratories report quantitative values and 2 report censored values (see Tab. 9). We could determine the certified value by simply calculating the mean and standard deviation from the quantitative values. Yet, this proceeding would ignore the information from the 2 censored values, which indicate that the mass content is below 1 mg/kg. To take the information from all laboratories into account, we make use of the marginal likelihood for μ. We fit a normal distribution to the marginal likelihood. The mean and standard deviation of the fitted normal serve as estimates for the true property value (M) and the related uncertainty u_{ilc}, analogue to the proceeding for quantitative values only. Figure 4 shows the marginal likelihood for the mass content of Fe and the fitted normal distribution. Table 21 summarizes the estimated values.

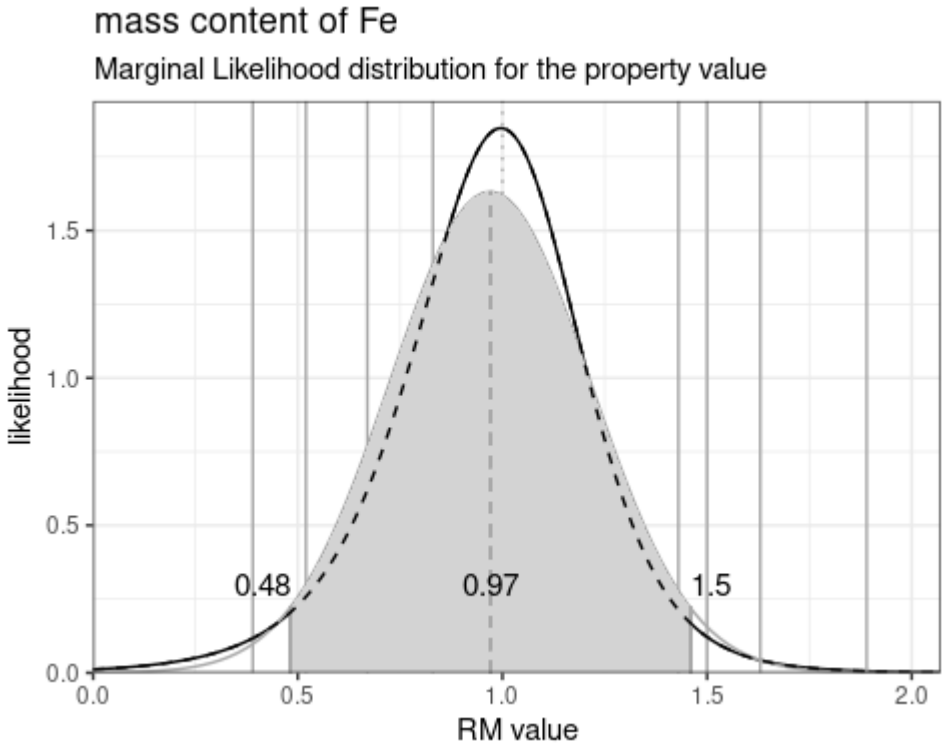


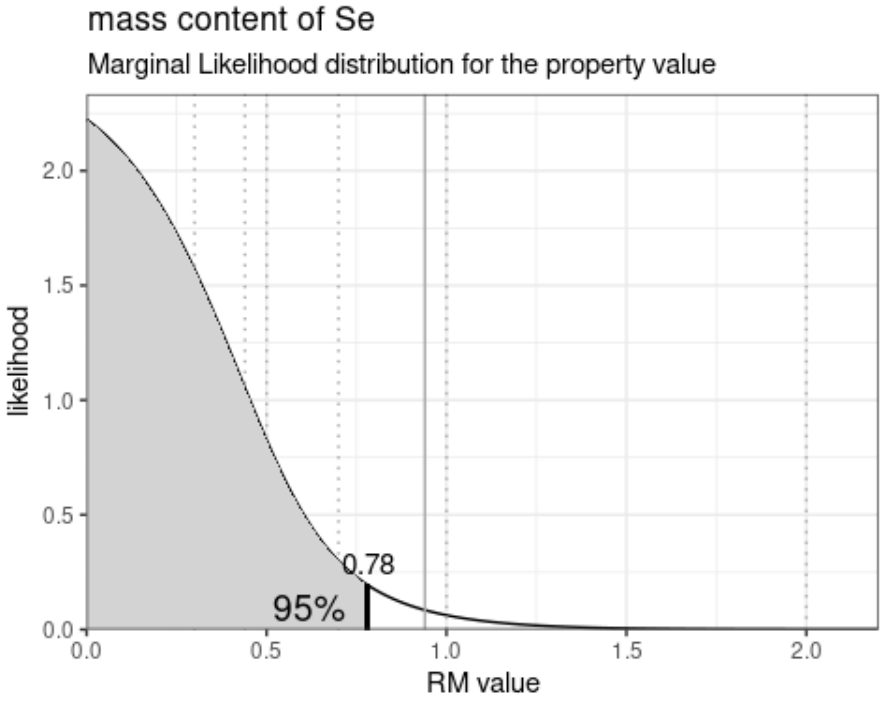
Figure 4: Marginal likelihood for the mass content of Fe (black line) and fitted normal distribution (gray area and line). The gray area shows the extended uncertainty intervall with *k*=2, which corresponds to approx. 95%. The gray vertical lines mark the quantitative values (solid) and censored values (dotted), provided by the laboratories.

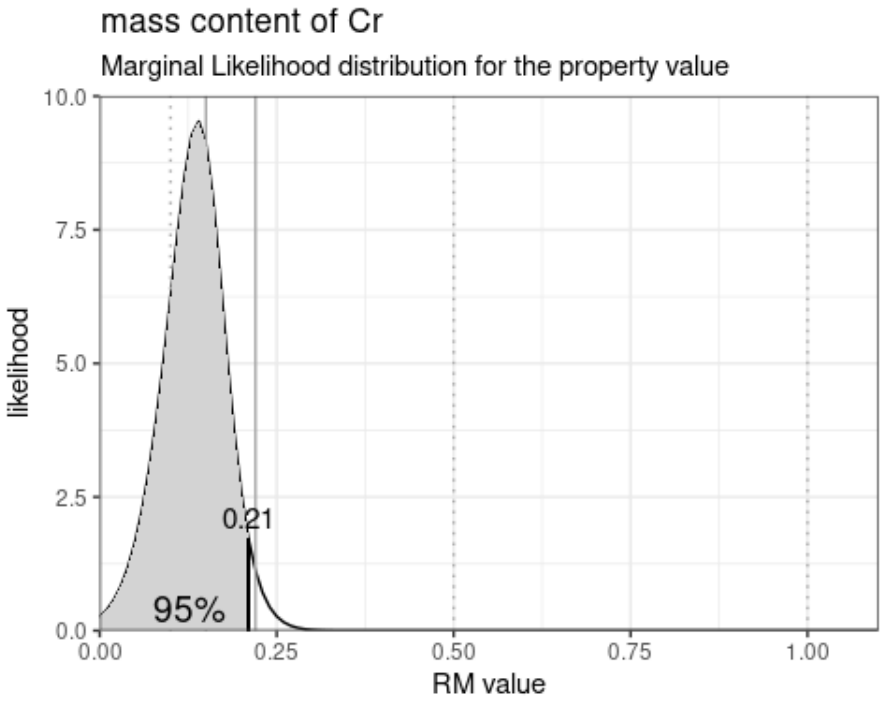
Table 21: Certified values and uncertainty calculation for Fe in BAM-M113

	M [mg/kg]	n_1	n_2	u_{ilc}	u_{bb} (Length)*	u_{bb} (Area)*	u_{comb}	U
Fe	0.97	8	2	0.25	0.011	0.011	0.25	0.50

*estimated as approx. mean of other elements

For Se, Cr, Mn, and As the number of quantitative values is below 5 and we estimate an upper limit instead of mean and standard deviation. The upper limit is estimated by calculating the 95% quantile of the marginal likelihood distribution (see Figure 5).





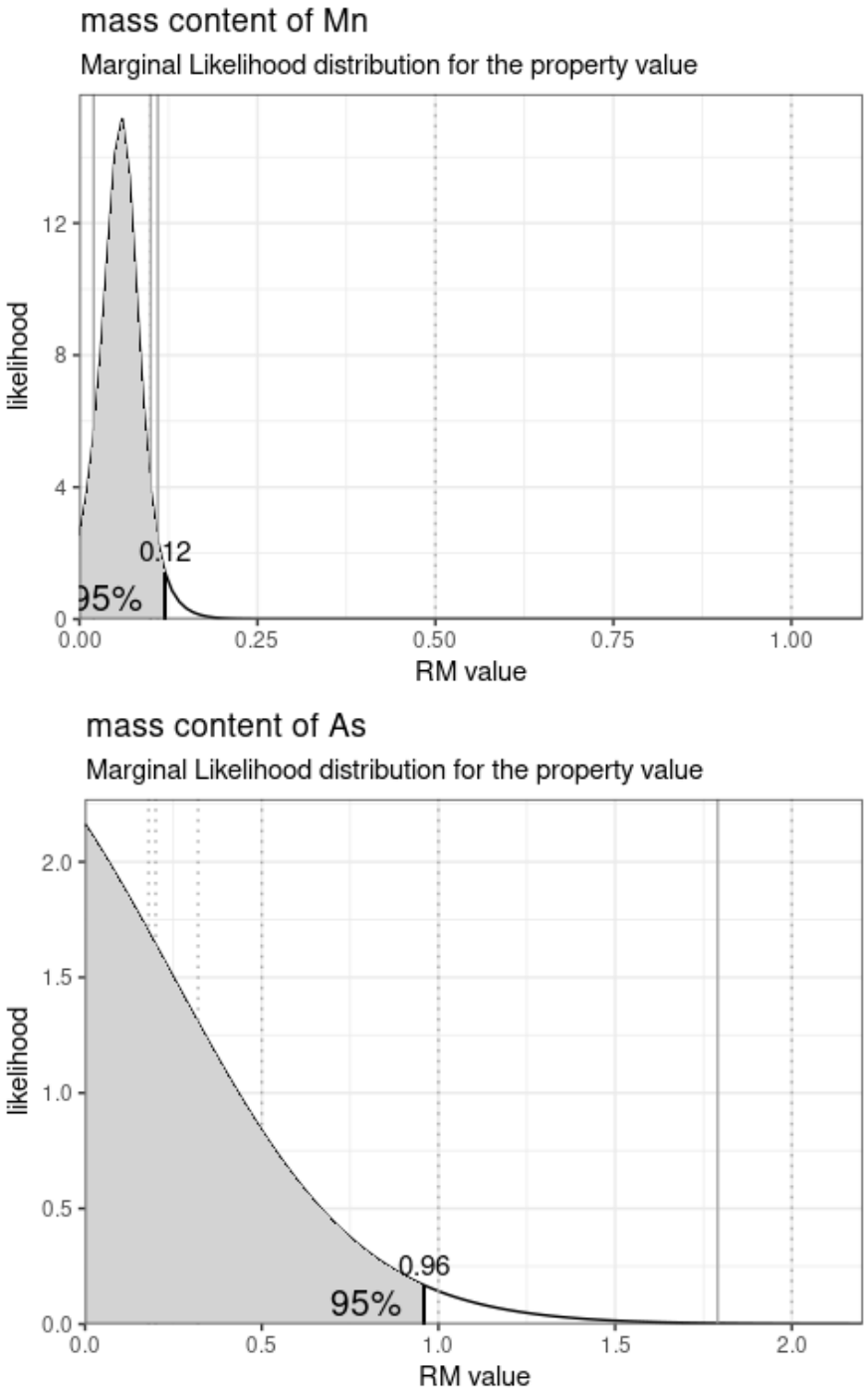


Figure 5: estimation of upper limit for Se, Cr, Mn, and As

Table 22 summarizes the 95% quantiles from the marginal likelihood functions. The true mass content is expected to be below this limit with 95% certainty. To account for possible wrong assumptions in the distribution of the measured values and for within sample uncertainty, we decided to take slightly larger values as certified limits and selected the next largest censored value from the laboratory values as certified limit.

Table 22: 95% quantiles (Q95) and certified limits for censored RM values.

	Q95 [mg/kg]	Certified limit [mg/kg]	Uncertainty*
Se	0.78	<1	0.05
Cr	0.21	<0.5	0.05
Mn	0.12	<0.5	0.05
As	0.96	<1	0.05

*Here the uncertainty refers to the probability of errors or in other words the significance level. A commonly used significance level is 0.05, which means that the probability for an error (i.e., the true value is outside of the given range) is 5%,

The calculated mass fractions and their resp. expanded uncertainties are given on Page 3 of this report. Rounding was done according to DIN 1333 [4].

In addition to the wet chemical characterization some of the laboratories analysed the material with spark emission spectrometry to check if there is agreement between SOES and wet chemistry. Tab. 23 shows the mean values of wet chemical and spark emission results as well as their standard deviations. The t-test (α = 0,05) showed no significant differences of the mean values for all elements except of Ag (no difference for α = 0,025).

Tab. 23: Comparison wet chemistry vs. SOES (BAM-M113)

Element	**Wet chemical analysis**			**Spark emission**			**t-test**	
	Mass fraction in %	**Std.-dev.** in %	***n***	**Mass fraction** in %	**Std.-dev.** in %	***n***	***t***	t_{cr}
Ca	0.124	0.005	12	0.126	0.009	12	0.452	2.074
Sn	1.047	0.024	11	1.048	0.025	11	0.096	2.086
Bi	0.0194	0.0012	10	0.0191	0.0010	12	0.635	2.086
Al	0.0145	0.0012	12	0.0148	0.0013	11	0.515	2.080
	in mg/kg	in mg/kg		in mg/kg	in mg/kg			
Ag	64.7	2.4	11	67.6	4.0	12	2.219	2.080
Cu	18.9	1.4	12	20.1	2.4	12	1.434	2.074
Sb	5.4	1.2	6	5.7	1.6	11	0.386	2.131
Fe	1.1	0.6	8	1.3	0.5	6	0.547	2.179

6. Instructions for users and stability

The certified reference material BAM-M113 is intended for the calibration and quality control of spark emission spectrometers used for the analysis of materials with similar matrix composition. It is also suitable for validation of wet chemical analysis methods.
The surface of the material should be cleaned by turning or milling before analysis.
If chips prepared from the compact material are used for wet chemical analysis, a minimum sample intake of 0.2 g has to be used.
The material will remain stable provided that it is not subjected to excessive heat (e.g, during preparation of the working surface).

7. Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

8. References

[1] ISO 17034, General requirements for the competence of reference material producers, 2016

[2] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation, 2015

[3] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability, 2017

[4] DIN 1333:1992-02 Zahlenangaben

9. Information on and purchase of the CRM

Certified reference material BAM-M113 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6 „Inorganic Reference Materials"
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 30 - 8104 2061
Fax: +49 30 – 8104 72061
E-mail: sales.crm@bam.de

Each disc of BAM-M113 will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM, https://www.bam.de.
Tel. +49 30 8104 1111

Annex 1: Difference between Sub-batch 2 and the other sub-batches for Ag, Al, and Cu

Mass fraction in mg/kg

Element	**Sub-Batches 1, 3 - 9 (*n* = 64)**		**Sub-batch 2 (*n* = 8)**	
	Mean	Std.-dev.	Mean	Std.-dev.
Al	145	3.3	137	1.6
Ag	65.7	0.37	64.3	0.30
Cu	19.1	0.14	18.7	0.14

Annex 2: Calculation of uncertainty contribution of potential inhomogeneity (between discs)
Silver in BAM-M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	65.89	65.85	65.58	65.49
1-40	65.90	66.12	65.54	65.66
2-1	64.46	64.70	63.92	64.06
2-42	64.39	64.62	64.08	64.00
3-1	65.89	65.99	65.38	65.60
3-42	65.54	65.87	65.44	65.29
4-1	65.41	65.34	65.02	64.94
4-42	65.00	65.37	64.92	64.86
5-1	66.37	66.04	65.76	65.48
5-42	66.25	65.97	65.86	65.52
6-1	66.08	65.86	65.65	65.87
6-42	66.43	65.58	65.58	65.69
7-1	66.72	65.63	65.44	65.54
7-41	65.72	65.78	65.91	65.42
8-1	65.99	65.51	65.45	65.06
8-42	66.22	65.96	65.53	65.30
9-1	65.77	65.68	65.73	65.23
9-42	65.52	65.64	65.74	65.43

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	17.1089792	17	1.006410541	10.111287	2.652E-11	1.8155404
Within groups	5.374802236	54	0.099533375			
Total	22.48378143	71				
within-sd	0.315489104			status:	inhomogeneous	
effective n	4.00					
s_{bb}	0.476150493					
u^*_{bb}	0.069201169					
u_{bb}	0.476150493					
u_{bb}(rel.)	0.726936018					

excl. Sub-batch 2

e of tion	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	3.707480207	15	0.247165347	2.50312971	0.00821976	1.88017458
Within groups	4.739641176	48	0.098742525			
Total	8.447121384	63				
within-sd	0.314233233			status:	inhomogeneous	
effective n	4.00					
	0.192628413					
	0.070985445					
	0.192628413					
	0.293401368					

Aluminium in BAM- M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	142.53	141.29	143.04	140.90
1-40	138.64	140.00	141.03	139.16
2-1	136.23	137.83	140.69	137.16
2-42	136.19	136.42	136.70	135.96
3-1	146.31	149.02	147.79	146.92
3-42	144.62	144.50	145.95	145.87
4-1	144.64	146.87	146.57	145.80
4-42	141.74	145.11	144.36	143.86
5-1	148.49	151.12	152.09	150.52
5-42	144.21	148.25	148.70	148.13
6-1	145.63	148.04	147.91	147.52
6-42	141.00	146.28	146.90	147.00
7-1	138.59	144.79	143.93	143.61
7-41	137.32	143.25	141.32	143.25
8-1	140.99	145.15	144.16	146.26
8-42	139.72	142.22	142.27	137.15
9-1	146.12	148.00	146.62	146.12
9-42	144.35	145.31	143.52	143.90

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	924.8149122	17	54.40087719	17.677209	2.9787E-16	1.8155404
Within groups	166.1827596	54	3.077458511			
Total	1090.997672	71				
within-sd	1.754268654			status:	inhomogeneous	
effective n	4.00					
s_{bb}	3.58201824					
u^*_{bb}	0.384791231					
u_{bb}	3.58201824					
u_{bb}(rel.)	2.491012521					

excl. Sub-batch 2

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between gro	521.4085785	15	34.7605719	10.779135	1.0848E-10	1.88017458
Within group	154.7904778	48	3.224801621			
Total	676.1990563	63				
within-sd	1.795773266			status:	inhomogeneous	
effective n	4.00					
s_{bb}	2.807835923					
u^*_{bb}	0.40566608					
u_{bb}	2.807835923					
u_{bb}(rel.)	1.941408205					

Bismuth in BAM- M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	190.13	190.84	189.95	189.04
1-40	190.48	190.63	189.75	190.28
2-1	189.69	191.64	188.88	189.50
2-42	189.74	190.93	189.22	188.89
3-1	190.52	190.53	189.23	189.21
3-42	189.48	190.45	189.11	190.08
4-1	191.13	190.94	188.97	189.83
4-42	190.69	190.20	189.22	189.90
5-1	191.44	190.49	188.74	189.50
5-42	191.40	191.24	190.03	190.23
6-1	191.71	189.66	189.06	189.83
6-42	191.84	189.13	189.29	189.85
7-1	191.28	189.80	189.04	189.40
7-41	191.33	189.73	188.76	190.48
8-1	191.29	189.40	188.33	188.14
8-42	191.03	190.28	189.34	190.35
9-1	190.03	189.08	188.56	189.35
9-42	189.45	190.24	189.39	189.46

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	8.186237692	17	0.481543394	0.56938545	0.89974523	1.8155404
Within groups	45.66913863	54	0.845724789			
Total	53.85537632	71				
within-sd	0.919632965			status:	homogeneous	
effective n	5.00					
s_{bb}	0					
u^*_{bb}	0.180421624					
u_{bb}	0.180421624					
u_{bb}(rel.)	0.094920584					

excl. Sub-batch 2

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	7.919073558	15	0.527938237	0.6493904	0.8184921	1.8801746
Within groups	39.02280486	48	0.812975101			
Total	46.94187842	63				
within-sd	0.901651319			status:	homogeneous	
effective n	4.00					
	0					
	0.203683485					
	0.203683485					
	0.107223087					

Calcium in BAM- M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	1243.9	1286.4	1234.9	1294.2
1-40	1242.9	1276.0	1243.3	1274.0
2-1	1243.9	1247.4	1208.7	1256.3
2-42	1203.5	1220.6	1231.9	1251.6
3-1	1231.8	1235.6	1261.7	1283.6
3-42	1221.5	1254.1	1259.1	1231.4
4-1	1221.7	1207.0	1258.1	1253.4
4-42	1245.7	1211.3	1241.4	1235.2
5-1	1218.3	1223.7	1263.3	1259.3
5-42	1270.2	1218.2	1249.0	1261.7
6-1	1225.7	1240.8	1281.6	1284.7
6-42	1291.7	1248.0	1257.2	1245.6
7-1	1285.4	1229.1	1247.0	1260.0
7-41	1260.2	1239.2	1313.1	1238.8
8-1	1260.1	1247.2	1293.0	1234.4
8-42	1269.1	1247.6	1289.9	1203.4
9-1	1218.6	1244.4	1303.5	1209.0
9-42	1234.5	1243.3	1306.9	1251.3

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	8748.916567	17	514.642151	0.71899324	0.77004847	1.8155404
Within groups	38652.2081	54	715.7816315			
Total	47401.12467	71				
within-sd	26.7540956			status:	homogeneous	
effective n	5.00					
s_{bb}	0					
u^*_{bb}	5.24885205					
u_{bb}	5.24885205					
u_{bb}(rel.)	0.415636382					

excl. Sub-batch 2

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	5936.100603	15	395.7400402	0.5259181	0.9131744	1.8801746
Within groups	36118.78612	48	752.4747108			
Total	42054.88672	63				
within-sd	27.4312725			status:	homogeneous	
effective n	4.00					
	0					
	6.196738197					
	6.196738197					
	0.495019733					

Copper in BAM- M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	19.171	19.053	19.142	18.986
1-40	19.103	19.174	19.207	19.011
2-1	18.533	18.808	18.860	18.555
2-42	18.788	18.865	18.686	18.656
3-1	18.888	19.205	18.928	18.781
3-42	18.981	19.074	18.955	18.990
4-1	18.920	19.067	18.844	18.793
4-42	18.904	19.180	18.871	18.848
5-1	19.195	19.244	19.157	19.024
5-42	19.119	19.220	19.038	19.020
6-1	19.339	19.166	19.014	18.992
6-42	19.138	19.077	19.067	19.136
7-1	19.078	19.160	19.041	18.989
7-41	19.049	19.223	18.857	19.099
8-1	19.231	19.222	19.015	19.220
8-42	19.223	19.160	19.086	18.768
9-1	19.276	19.196	19.013	19.010
9-42	19.251	19.151	18.904	19.049

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	1.228723122	17	0.072277831	4.47875835	1.2136E-05	1.8155404
Within groups	0.87144752	54	0.016137917			
Total	2.100170642	71				
within-sd	0.127035102			status:	inhomogeneous	
effective n	5.00					
s_{bb}	0.105962176					
u^*_{bb}	0.024922855					
u_{bb}	0.105962176					
u_{bb}(rel.)	0.556030727					

excl. Sub-batch 2

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.359776126	15	0.023985075	1.51970723	0.13584467	1.88017458
Within groups	0.75756934	48	0.015782695			
Total	1.117345466	63				
within-sd	0.125629195			status:	homogeneous	
effective n	4.00					
s_{bb}	0.045283497					
u^*_{bb}	0.028379698					
u_{bb}	0.045283497					
u_{bb}(rel.)	0.237496507					

Tin in BAM- M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	10249.1	10224.2	10218.1	10158.1
1-40	10183.7	10275.6	10252.4	10186.1
2-1	10146.8	10282.4	10353.1	10224.6
2-42	10264.9	10326.8	10244.1	10242.5
3-1	10187.9	10323.5	10238.2	10181.0
3-42	10180.7	10257.2	10252.8	10233.3
4-1	10248.2	10344.4	10244.9	10241.4
4-42	10245.0	10383.0	10251.9	10246.6
5-1	10282.4	10356.4	10326.3	10270.0
5-42	10254.5	10332.5	10272.2	10227.3
6-1	10321.6	10296.9	10250.8	10200.3
6-42	10222.5	10231.5	10272.8	10263.6
7-1	10237.5	10277.9	10282.0	10219.7
7-41	10166.1	10267.1	10214.2	10297.3
8-1	10200.9	10243.4	10218.9	10323.0
8-42	10224.5	10215.0	10244.1	
9-1	10255.3	10238.8	10193.2	
9-42	10246.2	10205.3	10162.2	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	44782.70476	17	2634.276751	1.07331814	0.40341101	1.827147
Within groups	125170.8222	51	2454.329847			
Total	169953.527	68				
within-sd	49.54119344			status:	homogeneous	
effective n	4.00					
s_{bb}	6.707214462					
u^*_{bb}	11.02304102					
u_{bb}	11.02304102					
u_{bb}(rel.)	0.107561031					

excl. Sub-batch 2

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	42993.5003	15	2866.233353	1.3224783	0.2290352	1.8948747
Within groups	97529.39043	45	2167.319787			
Total	140522.8907	60				
within-sd	46.55448193			status:	homogeneous	
effective n	4.00					
s_{bb}	13.21848673					
u^*_{bb}	10.68773982					
u_{bb}	13.21848673					
u_{bb}(rel.)	0.129003454					

Antimony in BAM- M113 (mass fraction in mg/kg):
incl. Sub-batch 2

Sample	1	2	3	4
1-1	8.0243	7.5511	8.0684	7.2267
1-40	7.8169	7.3063	7.7487	7.7960
2-1	7.6340	7.5268	7.6593	7.6067
2-42	7.9296	7.6932	7.6112	7.5363
3-1	7.3902	7.4854	6.9796	7.4018
3-42	7.5384	7.6318	7.0434	7.1481
4-1	7.9940	8.0585	7.6346	7.5091
4-42	8.1274	7.6976	7.5837	7.8427
5-1	7.8469	8.1777	7.1858	7.9210
5-42	7.8217	7.7252	7.5298	7.6205
6-1	7.7760	7.5804	7.6411	7.9767
6-42	7.5570	7.5499	6.8447	7.9653
7-1	7.7787	7.1789	8.0503	7.8269
7-41	8.0161	7.5114	7.5165	7.6825
8-1	7.3284	7.3217	7.1441	7.3122
8-42	7.0364	7.6067	7.3609	7.2873
9-1	7.6643	7.6127	7.3128	7.6521
9-42	7.4464	7.4288	7.5903	7.3484

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2.225883284	17	0.130934311	1.88157756	0.04063272	1.8155404
Within groups	3.757725934	54	0.069587517			
Total	5.983609218	71				
within-sd	0.26379446			status:	inhomogeneous	
effective n	4.00					
s_{bb}	0.123841424					
u^*_{bb}	0.057862172					
u_{bb}	0.123841424					
u_{bb}(rel.)	1.631471324					

excl. Sub-batch 2

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2.17994106	15	0.145329404	1.9056406	0.0464963	1.8801746
Within groups	3.660612285	48	0.076262756			
Total	5.840553345	63				
within-sd	0.276157122			status:	inhomogeneous	
effective n	4.00					
	0.131402671					
	0.062384032					
	0.131402671					
	1.73276204					

Annex 3: Calculation of uncertainty contribution of potential inhomogeneity (area)
Silver in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	65.805	65.863	65.477	65.491
Inner circle	65.169	65.368	65.028	65.121
Centre	65.228	65.469	64.869	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.587327061	2	0.29366353	6.3777218	0.0220715	4.4589701
Within groups	0.368361667	8	0.046045208			
Total	0.955688727	10				
within-sd	0.214581472			status:	inhomogeneous	
effective n	4.00					
s_{bb}	0.248806311					
u^*_{bb}	0.075866007					
u_{bb}	0.248806311					
u_{bb}(rel.)	0.380675464					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	64.02	64.08	64.003	64.258
Inner circle	63.837	64.049	63.667	63.55
Centre	63.409	63.853	63.63	64.107

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.287368667	2	0.143684333	2.8689799	0.1086734	4.2564947
Within groups	0.45073825	9	0.050082028			
Total	0.738106917	11				
within-sd	0.223790142			status:	homogeneous	
effective n	4.00					
s_{bb}	0.152972469					
u^*_{bb}	0.07682593					
u_{bb}	0.152972469					
u_{bb}(rel.)	0.239498793					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	64.978	65.4	65.272	64.943
Inner circle	64.593	64.643	64.983	64.828
Centre	64.514	64.739	65.061	64.856

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.369181167	2	0.184590583	4.1298256	0.0533884	4.2564947
Within groups	0.4022725	9	0.044696944			
Total	0.771453667	11				
within-sd	0.211416519			status:	homogeneous	
effective n	4.00					
s_{bb}	0.18701179					
u^*_{bb}	0.072578133					
u_{bb}	0.18701179					
u_{bb}(rel.)	0.28815006					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	65.629	65.873	66.273	65.782
Inner circle	65.432	65.491	65.471	65.869
Centre	65.466	65.418	65.646	65.722

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.281465167	2	0.140732583	3.0610343	0.0967923	4.2564947
Within groups	0.4137795	9	0.0459755			
Total	0.695244667	11				
within-sd	0.214418982			status:	homogeneous	
effective n	4.00					
s_{bb}	0.153913193					
u^*_{bb}	0.073608862					
u_{bb}	0.153913193					
u_{bb}(rel.)	0.234364158					

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	65.962	65.436	65.589	65.448
Inner circle	65.783	65.561	65.245	64.98
Centre	65.499	65.809	65.392	65.498

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.100147167	2	0.050073583	0.6922589	0.525234	4.2564947
Within groups	0.6510025	9	0.072333611			
Total	0.751149667	11				
within-sd	0.268949086			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.092328749					
u_{bb}	0.092328749					
u_{bb}(rel.)	0.140923705					

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	65.824	65.432	65.464	65.919
Inner circle	64.984	66.591	65.833	65.214
Centre	65.568	65.622	65.768	66.035

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.021937167	2	0.010968583	0.0528487	0.9488156	4.2564947
Within groups	1.8679225	9	0.207546944			
Total	1.889859667	11				
within-sd	0.455573204			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.156395786					
u_{bb}	0.156395786					
u_{bb}(rel.)	0.238089427					
Median	0.23879411					

Aluminium in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	138.387	139.436	141.149	141.869
Inner circle	141.826	141.146	142.162	142.853
Centre	140.903	140.936	142.184	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6.506232682	2	3.253116341	2.5674911	0.1376075	4.4589701
Within groups	10.1363275	8	1.267040938			
Total	16.64256018	10				
within-sd	1.12562913			status:	homogeneous	
effective n	4.00					
s_{bb}	0.704640938					
u^*_{bb}	0.397969995					
u_{bb}	0.704640938					
u_{bb}(rel.)	0.499257301					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	134.696	134.534	138.683	134.96
Inner circle	136.591	136.109	137.33	135.845
Centre	136.182	136.431	133.933	134.916

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2.539791167	2	1.269895583	0.6666749	0.5370395	4.2564947
Within groups	17.1433785	9	1.904819833			
Total	19.68316967	11				
within-sd	1.380152105			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.47379866					
u_{bb}	0.47379866					
u_{bb}(rel.)	0.348763897					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	145.157	145.609	148.538	147.429
Inner circle	147.005	146.947	146.035	146.172
Centre	147.524	146.42	142.601	144.316

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	5.239888667	2	2.619944333	1.3754289	0.3011468	4.2564947
Within groups	22.67671825	9	1.904819833			
Total	27.91660692	11				
within-sd	1.380152105			status:	homogeneous	
effective n	4.00					
s_{bb}	0.422825171					
u^*_{bb}	0.47379866					
u_{bb}	0.47379866					
u_{bb}(rel.)	0.32419525					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	149.578	148.293	146.302	147.587
Inner circle	147.007	148.814	151.073	144.909
Centre	145.265	148.68	149.849	147.385

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.060732167	2	0.030366083	0.0159417	0.9842124	4.2564947
Within groups	37.8229995	9	1.904819833			
Total	37.88373167	11				
within-sd	1.380152105			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.47379866					
u_{bb}	0.47379866					
u_{bb}(rel.)	0.320361152					

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	141.495	143.569	142.941	144.956
Inner circle	143.571	144.087	139.245	135.515
Centre	140.675	140.988	138.156	141.507

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	20.64337817	2	10.32168908	5.418722	0.0285368	4.2564947
Within groups	61.53008675	9	1.904819833			
Total	82.17346492	11				
within-sd	1.380152105			status:	inhomogeneous	
effective n	4.00					
s_{bb}	1.450592056					
u^*_{bb}	0.47379866					
u_{bb}	1.450592056					
u_{bb}(rel.)	1.025935839					

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	143.914	136.684	138.981	146.879
Inner circle	136.756	144.159	145.38	144.489
Centre	145.817	149.015	144.969	141.887

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	30.79703267	2	15.39851633	8.0839752	0.0097786	4.2564947
Within groups	137.857595	9	1.904819833			
Total	168.6546277	11				
within-sd	1.380152105			status:	inhomogeneous	
effective n	4.00					
s_{bb}	1.836688358					
u^*_{bb}	0.47379866					
u_{bb}	1.836688358					
u_{bb}(rel.)	1.282208135					
Median	0.424010599					

Bismuth in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	190.027	190.827	191.31	191.193
Inner circle	189.781	190.043	189.799	189.975
Centre	189.665	189.552	188.337	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4.828515765	2	2.414257883	9.0199	0.0089086	4.4589701
Within groups	2.141272417	8	0.267659052			
Total	6.969788182	10				
within-sd	0.51735776			status:	inhomogeneous	
effective n	4.00					
s_{bb}	0.732563791					
u^*_{bb}	0.18291359					
u_{bb}	0.732563791					
u_{bb}(rel.)	0.385583059					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	190.968	190.529	192.846	191.67
Inner circle	189.88	189.811	191.156	188.519
Centre	189.267	189.925	190.167	189.649

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	7.781733167	2	3.890866583	5.0070092	0.0345349	4.2564947
Within groups	6.99375575	9	0.777083972			
Total	14.77548892	11				
within-sd	0.881523665			status:	inhomogeneous	
effective n	4.00					
s_{bb}	0.882295672					
u^*_{bb}	0.302622247					
u_{bb}	0.882295672					
u_{bb}(rel.)	0.463474362					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	191.162	191.114	190.528	190.559
Inner circle	190.135	189.992	189.364	190.355
Centre	190.387	189.49	191.202	190.588

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	1.546812167	2	0.773406083	2.8958825	0.1069058	4.2564947
Within groups	2.4036385	9	0.267070944			
Total	3.950450667	11				
within-sd	0.516789072			status:	homogeneous	
effective n	4.00					
s_{bb}	0.35578615					
u^*_{bb}	0.177410858					
u_{bb}	0.35578615					
u_{bb}(rel.)	0.186856258					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	191.878	191.398	191.075	191.904
Inner circle	191.374	189.962	190.404	190.151
Centre	190.551	189.675	190.977	190.874

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	3.044564667	2	1.522282333	5.0529617	0.0337937	4.2564947
Within groups	2.71138825	9	0.301265361			
Total	5.755952917	11				

within-sd	0.548876453	status:	inhomogeneous
effective n	4.00		
s_{bb}	0.552498184		
u^*_{bb}	0.188426281		
u_{bb}	0.552498184		
u_{bb}(rel.)	0.289490508		

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	190.044	189.749	190.339	189.87
Inner circle	189.257	190.815	189.285	191.234
Centre	189.532	191.176	189.469	190.614

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.084120167	2	0.042060083	0.0692762	0.9335616	4.2564947
Within groups	5.4642285	9	0.6071365			
Total	5.548348667	11				

within-sd	0.779189643	status:	homogeneous
effective n	4.00		
s_{bb}	0		
u^*_{bb}	0.267491538		
u_{bb}	0.267491538		
u_{bb}(rel.)	0.140699613		

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	189.686	190.586	190.583	191.765
Inner circle	191.675	191.805	190.612	189.79
Centre	190.799	190.659	189.176	193.907

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.4764305	2	0.23821525	0.1279431	0.8814755	4.2564947
Within groups	16.75695575	9	1.861883972			
Total	17.23338625	11				

within-sd	1.364508693	status:	homogeneous
effective n	4.00		
s_{bb}	0		
u^*_{bb}	0.468428362		
u_{bb}	0.468428362		
u_{bb}(rel.)	0.245352896		
Median	0.267421702		

Calcium in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	1327.515	1304.374	1274.979	1268.605
Inner circle	1283.549	1286.814	1274.084	1251.903
Centre	1323.553	1350.059	1270.138	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2826.252315	2	1413.126158	1.7957253	0.2268866	4.4589701
Within groups	6295.511472	8	786.9389341			
Total	9121.763788	10				
within-sd	28.05243187			status:	homogeneous	
effective n	4.00					
s_{bb}	12.5118666					
u^*_{bb}	9.918032403					
u_{bb}	12.5118666					
u_{bb}(rel.)	0.968531419					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	1253.972	1276.774	1229.917	1291.867
Inner circle	1262.484	1294.761	1246.077	1313.395
Centre	1294.97	1276.144	1320.075	1316.786

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	3050.928463	2	1525.464232	2.1965877	0.1671534	4.2564947
Within groups	6250.229923	9	694.4699914			
Total	9301.158386	11				
within-sd	26.35279855			status:	homogeneous	
effective n	4.00					
s_{bb}	14.41348535					
u^*_{bb}	9.046771434					
u_{bb}	14.41348535					
u_{bb}(rel.)	1.124792399					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	1276.544	1274.254	1262.22	1290.929
Inner circle	1286.037	1285.755	1317.468	1275.785
Centre	1291.298	1321.125	1309.144	1352.194

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	3699.077405	2	1849.538702	4.9399012	0.0356536	4.2564947
Within groups	3369.672348	9	374.4080387			
Total	7068.749753	11				
within-sd	19.34962632			status:	inhomogeneous	
effective n	4.00					
s_{bb}	19.2037149					
u^*_{bb}	6.642620757					
u_{bb}	19.2037149					
u_{bb}(rel.)	1.482649688					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	1248.46	1333.133	1328.466	1277.915
Inner circle	1309.869	1258.486	1258.866	1344.738
Centre	1287.208	1307.974	1276.171	1350.708

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	327.3845165	2	163.6922582	0.1084975	0.8983368	4.2564947
Within groups	13578.47155	9	1508.719061			
Total	13905.85607	11				
within-sd	38.84223296			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	13.33432587					
u_{bb}	13.33432587					
u_{bb}(rel.)	1.026902658					

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	1307.773	1273.347	1272.463	1247.087
Inner circle	1290.335	1265.985	1276.903	1288.621
Centre	1299.589	1335.552	1330.372	1308.215

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4455.513258	2	2227.756629	6.377854	0.018837	4.2564947
Within groups	3143.660805	9	349.295645			
Total	7599.174063	11				
within-sd	18.68945277			status:	inhomogeneous	
effective n	4.00					
s_{bb}	21.67060788					
u^*_{bb}	6.415986794					
u_{bb}	21.67060788					
u_{bb}(rel.)	1.678131347					

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	1317.504	1312.115	1277.062	1276.959
Inner circle	1214.844	1293.418	1314.119	1287.96
Centre	1329.216	1273.766	1328.992	1361.692

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4257.209975	2	2128.604988	1.7309347	0.2311889	4.2564947
Within groups	11067.68757	9	1229.743063			
Total	15324.89754	11				
within-sd	35.06769258			status:	homogeneous	
effective n	4.00					
s_{bb}	14.99051304					
u^*_{bb}	12.03854683					
u_{bb}	14.99051304					
u_{bb}(rel.)	1.154030217					
Median	1.139411308					

Copper in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	18.682	18.775	18.86	18.882
Inner circle	18.904	18.851	18.843	18.945
Centre	18.775	18.738	18.849	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.021492379	2	0.010746189	2.2540414	0.1673389	4.4589701
Within groups	0.038140167	8	0.004767521			
Total	0.059632545	10				
within-sd	0.069047236			status:	homogeneous	
effective n	4.00					
s_{bb}	0.038660925					
u^*_{bb}	0.024411884					
u_{bb}	0.038660925					
u_{bb}(rel.)	0.205511131					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	18.392	18.421	18.73	18.41
Inner circle	18.538	18.523	18.526	18.406
Centre	18.452	18.53	18.289	18.452

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.010616667	2	0.005308333	0.3959071	0.6842378	4.2564947
Within groups	0.12067225	9	0.013408028			
Total	0.131288917	11				
within-sd	0.115793039			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.039751116					
u_{bb}	0.039751116					
u_{bb}(rel.)	0.215191747					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	18.675	18.717	18.895	18.839
Inner circle	18.687	18.722	18.643	18.649
Centre	18.759	18.695	18.54	18.518

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.049445167	2	0.024722583	2.8807578	0.1078952	4.2564947
Within groups	0.07723775	9	0.008581972			
Total	0.126682917	11				
within-sd	0.092638935			status:	homogeneous	
effective n	4.00					
s_{bb}	0.063522852					
u^*_{bb}	0.031802439					
u_{bb}	0.063522852					
u_{bb}(rel.)	0.339786764					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	19.047	18.964	18.783	18.886
Inner circle	18.747	18.962	19.06	18.761
Centre	18.837	18.879	19.056	18.861

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.002943167	2	0.001471583	0.0953278	0.9099805	4.2564947
Within groups	0.13893375	9	0.015437083			
Total	0.141876917	11				

within-sd	0.12424606			status:	homogeneous
effective n	4.00				
s_{bb}	0				
u^*_{bb}	0.042652992				
u_{bb}	0.042652992				
u_{bb}(rel.)	0.225634427				

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	18.724	18.825	18.751	18.981
Inner circle	18.756	18.855	18.546	18.298
Centre	18.714	18.604	18.363	18.63

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.136992667	2	0.068496333	2.1202776	0.1760003	4.2564947
Within groups	0.29074825	9	0.032305361			
Total	0.427740917	11				

within-sd	0.179736922			status:	homogeneous
effective n	4.00				
s_{bb}	0.095119625				
u^*_{bb}	0.061702701				
u_{bb}	0.095119625				
u_{bb}(rel.)	0.509462523				

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	18.783	18.362	18.618	19.08
Inner circle	18.484	18.839	18.873	18.839
Centre	18.864	19.165	18.774	18.487

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.0251415	2	0.01257075	0.1863387	0.8331147	4.2564947
Within groups	0.6071565	9	0.067461833			
Total	0.632298	11				

within-sd	0.259734159			status:	homogeneous
effective n	4.00				
s_{bb}	0				
u^*_{bb}	0.089165314				
u_{bb}	0.089165314				
u_{bb}(rel.)	0.475193533				
Median	0.282710595				

Antimony in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	7.511	7.457	7.546	7.694
Inner circle	7.554	7.795	7.181	7.061
Centre	7.569	7.258	7.326	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.06547222	2	0.03273611	0.6133611	0.5651584	4.4589701
Within groups	0.426973417	8	0.053371677			
Total	0.492445636	10				
within-sd	0.231023109			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.081679004					
u_{bb}	0.081679004					
u_{bb}(rel.)	1.095945662					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	8.081	7.659	7.078	7.285
Inner circle	7.297	7.47	7.593	7.37
Centre	7.732	8.341	7.597	7.401

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.239536167	2	0.119768083	0.9560316	0.4202525	4.2564947
Within groups	1.1274865	9	0.125276278			
Total	1.367022667	11				
within-sd	0.353943891			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.121506999					
u_{bb}	0.121506999					
u_{bb}(rel.)	1.603982216					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	7.227	7.691	8.177	7.836
Inner circle	7.695	7.733	7.473	7.975
Centre	8.391	7.728	7.918	7.69

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.1134035	2	0.05670175	0.5648676	0.587354	4.2564947
Within groups	0.9034255	9	0.100380611			
Total	1.016829	11				
within-sd	0.316828993			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.108765659					
u_{bb}	0.108765659					
u_{bb}(rel.)	1.395415466					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	7.512	7.427	7.152	7.294
Inner circle	7.695	7.755	7.796	7.839
Centre	7.539	7.462	7.599	7.395

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.37085	2	0.185425	15.237315	0.0012902	4.2564947
Within groups	0.10952225	9	0.012169139			
Total	0.48037225	11				
within-sd	0.11031382			status:	inhomogeneous	
effective n	4.00					
s_{bb}	0.208120074					
u^*_{bb}	0.03787013					
u_{bb}	0.208120074					
u_{bb}(rel.)	2.760670856					

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	7.191	7.101	6.988	7.428
Inner circle	6.994	7.756	7.551	8.111
Centre	7.195	7.433	7.479	7.206

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.373120167	2	0.186560083	2.0323661	0.1869128	4.2564947
Within groups	0.82615075	9	0.091794528			
Total	1.199270917	11				
within-sd	0.302976118			status:	homogeneous	
effective n	4.00					
s_{bb}	0.153920073					
u^*_{bb}	0.104010042					
u_{bb}	0.153920073					
u_{bb}(rel.)	2.088633063					

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	7.592	6.864	7.715	7.04
Inner circle	7.7	7.195	7.258	6.961
Centre	7.518	7.097	7.217	8.189

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.124013167	2	0.062006583	0.3675194	0.7023793	4.2564947
Within groups	1.5184485	9	0.1687165			
Total	1.642461667	11				
within-sd	0.410751141			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	0.141008617					
u_{bb}	0.141008617					
u_{bb}(rel.)	1.915314117					
Median	1.759648167					

Tin in BAM-M113 (mass fraction in mg/kg):

1				
	Result 1	Result 2	Result 3	Result 4
Outer circle	9927.916	9934.584	10022.944	10021.006
Inner circle	10002.77	10028.391	9985.956	10084.148
Centre	9980.621	9969.252	9973.718	

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6268.674656	2	3134.337328	1.8105857	0.2245744	4.4589701
Within groups	13848.94313	8	1731.117892			
Total	20117.61779	10				
within-sd	41.60670489			status:	homogeneous	
effective n	4.00					
s_{bb}	18.72978535					
u^*_{bb}	14.71019158					
u_{bb}	18.72978535					
u_{bb}(rel.)	0.187533273					

4				
	Result 1	Result 2	Result 3	Result 4
Outer circle	10043.127	9983.221	10172.13	10053.594
Inner circle	10116.266	10049.661	10083.603	10017.16
Centre	10060.178	10083.178	9960.779	9995.151

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4298.445578	2	2149.222789	0.5708961	0.5842183	4.2564947
Within groups	33881.83283	9	3764.648092			
Total	38180.27841	11				
within-sd	61.35672818			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	21.06342879					
u_{bb}	21.06342879					
u_{bb}(rel.)	0.209554996					

7				
	Result 1	Result 2	Result 3	Result 4
Outer circle	10045.836	10085.978	10161.022	10164.291
Inner circle	10067.593	10052.343	10054.062	10063.28
Centre	10103.638	10046.069	9663.203	9944.631

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	63991.81195	2	31995.90597	2.3037699	0.1556263	4.2564947
Within groups	124996.4897	9	13888.49886			
Total	188988.3017	11				
within-sd	117.8494754			status:	homogeneous	
effective n	4.00					
s_{bb}	67.28188299					
u^*_{bb}	40.45707957					
u_{bb}	67.28188299					
u_{bb}(rel.)	0.670294356					

11				
	Result 1	Result 2	Result 3	Result 4
Outer circle	10118.185	10138.504	9958.762	10075.362
Inner circle	10010.799	10080.425	10206.612	9823.7
Centre	9755.323	10060.774	10095.889	10046.98

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	13767.17825	2	6883.589126	0.3631618	0.7052159	4.2564947
Within groups	170591.4503	9	18954.60559			
Total	184358.6285	11				
within-sd	137.6757262			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	47.26332289					
u_{bb}	47.26332289					
u_{bb}(rel.)	0.471175275					

14				
	Result 1	Result 2	Result 3	Result 4
Outer circle	9967.485	10049.217	9996.564	10079.329
Inner circle	10010	10045.351	9606.273	9227.359
Centre	9777.292	9804.846	9571.992	9925.402

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	209273.9508	2	104636.9754	1.818623	0.2170977	4.2564947
Within groups	517827.3731	9	57536.37479			
Total	727101.3239	11				
within-sd	239.8674108			status:	homogeneous	
effective n	4.00					
	108.513364					
	82.34516863					
	108.513364					
	1.102954536					

18				
	Result 1	Result 2	Result 3	Result 4
Outer circle	9950.408	9346.679	9405.023	10063.288
Inner circle	8989.957	9837.523	9963.581	9854.901
Centre	10000.334	10128.151	9931.801	9598.967

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	153333.3642	2	76666.68208	0.5898872	0.574473	4.2564947
Within groups	1169715.378	9	129968.3754			
Total	1323048.742	11				
within-sd	360.5112694			status:	homogeneous	
effective n	4.00					
s_{bb}	0					
u^*_{bb}	123.7615446					
u_{bb}	123.7615446					
u_{bb}(rel.)	1.268583547					
Median	0.570734816					